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Journal of Research of the National Bureau of Standards Vol. 62, No. 5, May 1959 Research Paper 2950

Mean Absolute Value and Standard Deviation of the Phase of a Constant Vector Plus a Rayleigh-Distributed Vector

J. Ralph Johler and Lillie C. Walters

The mean absolute value of the phase and the standard deviation of the phase of a constant vector plus a Rayleigh-distributed vector are determined by an evaluation of the first and second moment integrals of the probability distribution for various values of average relative intensity of the random Rayleigh-distributed component. The results of a quadrature evaluation of the integrals are tabulated over a wide range of values of average relative intensity ($k^2=0.010$ to 1,000).

1. Introduction to the Problem

Let $E_s(t)$ be a random vector whose amplitude, $|E_s(t)|$, is Rayleigh distributed in time and whose amplitude, $|E_s(t)|$, and phase angle, Arg $E_s(t)$, are independently distributed. Rice [1][1] has introduced the concept of a constant vector, E_o, plus a randomly distributed vector, $E_s(t)$, to describe electric currents or electric fields, $E(t)=E_o+E_s(t)$, subject to various natural fluctuations. Norton has presented tables of the cumulative distribution [2] of the amplitude, $|E(t)|$, and its phase [3], $\Omega=\text{Arg}\,E(t)$, with the relative intensity, $k^2=|E_r|^2/|E_o|^2$, as a parameter, where $|E_r|$ is the root mean square value of the amplitude $|E_s(t)|$. In connection with some recent studies of ionosphere roughness, Norton [4] obtained the following probability density function[2] of the phase, $p(\Omega)$, by integrating over the joint probability distribution given by Rice [1] with respect to amplitude, E, the time derivative of the amplitude, E', and the time derivative of the phase, Ω':

$$2\pi\, p(\Omega)=\{1+\sqrt{\pi}\, z\, \exp(z^2)\,[1+\text{erf}(z)]\}\,\exp(-1/k^2) \quad (1)$$

where

$$z=\frac{\cos\,\Omega}{k}. \quad (2)$$

The phase fluctuations are especially important in the performance evaluation of radio navigation and phase modulation systems since the behavior of such systems is dependent upon the behavior of the argument or phase, Ω, of the vector, $E(t)$.

The determination of the mean absolute value, $\overline{|\Omega|}$, of the phase, $\Omega=\arg E(t)$, and the corresponding standard deviation, σ_Ω, of a constant vector, plus a Rayleigh-distributed vector, $E(t)$, by an evaluation of the first and second moment integrals of the probability density function, $p(\Omega)$, for various values of the random Rayleigh-distributed component of average relative intensity, k^2, is the object of this paper.

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] It is of interest to note that H. Bremmer has independently derived the expression for $p(\Omega)$ (private communication).

2. Theory

The evaluation of the mean absolute value, $\overline{|\Omega|}$, of the vector argument or "phase," Ω, and the corresponding variance, σ_Ω^2, integrals,

$$\overline{|\Omega|}=2\int_0^\pi \Omega\, p(\Omega)\, d\Omega, \quad (3)$$

and

$$\sigma_\Omega^2=2\int_0^\pi \Omega^2 p(\Omega)\, d\Omega, \quad (4)$$

as a function of k^2 is the prime task of this paper. The probability density function, $p(\Omega)$, is symmetric about zero, $\Omega=0$, and hence the mean, $\overline{\Omega}$, is zero. The probability distribution, $p(\Omega)$, involves the error function,

$$\text{erf}(z)=\frac{2}{\sqrt{\pi}}\int_0^z e^{-u^2}du, \quad (5)$$

which can be evaluated by the following convergent series:

$$\text{erf}(z)=\frac{2}{\sqrt{\pi}}\left[z-\frac{z^3}{1!3}+\frac{z^5}{2!5}-\frac{z^7}{3!7}+\cdots\right]. \quad (6)$$

It is frequently more efficient for large values of z, $(z>1)$ to use the asymptotic expansion for real values of z,

$$1-\text{erf}(z)=\frac{1}{z\sqrt{\pi}}\,\exp(-z^2)\left[1-\frac{1}{2z^2}+\frac{1\cdot3}{(2z^2)^2}-\frac{1\cdot3\cdot5}{(2z^2)^3}+\frac{1\cdot3\cdot5\cdot7}{(2z^2)^4}-\cdots\right]. \quad (7)$$

The mean absolute value, $\overline{|\Omega|}$, and the variance, σ_Ω^2, integrals can be represented in the theory of Gaussian quadrature [5] as a finite sum,

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$$\overline{[\Omega]}=\frac{1}{\pi}\exp\,(-1/k^2)\int_0^\pi \Omega p_0(\Omega)d\Omega$$

$$=\frac{1}{\pi}\exp\,(-1/k^2)\sum_{m=1}^{M} W_m\Omega_m p_0(\Omega_m)+\epsilon_M, \quad (8)$$

$$\sigma_\Omega^2=\frac{1}{\pi}\exp\,(-1/k^2)\int_0^\pi \Omega^2 p_0(\Omega)d\Omega$$

$$=\frac{1}{\pi}\exp\,(-1/k^2)\sum_{m=1}^{M} W_m\Omega^2{}_m p_0(\Omega_m)+\epsilon'_M, \quad (9)$$

$m=1, 2, 3 \ . \ . \ . \ M$,

where ϵ_M and ϵ'_M are error terms which can in general be made arbitrarily small by increasing M,

$$p_0(\Omega)=2\pi\exp\,(1/k^2)p(\Omega), \quad (10)$$

$$\Omega_m=\frac{1}{2}[\Omega_b-\Omega_a]x_m+\frac{1}{2}[\Omega_b+\Omega_a], \quad (11)$$

and where $\Omega_b=\pi$, and $\Omega_a=0$, are the upper and lower limits of integration, respectively. The weight functions can be determined from the limits of integration,

$$W_m=\frac{1}{2}[\Omega_b-\Omega_a]H_m. \quad (12)$$

Thus, the integer, M, and the limits of integration, Ω_a, Ω_b, determine the particular values of the integrand to be calculated in the quadrature. The "universal" constants of the theory of Gaussian quadrature, H_m, x_m, can be determined for any given $f(x)$ and various M,

$$\int_{-1}^{1} f(x)dx=\sum_{m=1}^{M} H_m f(x_m). \quad (13)$$

The abscissas, x_m, are the roots of the Legendre polynomials defined by,

$$\frac{d^m}{dx^m}(x^2-1)^m-2^m m!P_m(x)=0$$

$$P_0(x)=1$$

$$P_1(x)=x$$

$$P_2(x)=\frac{3}{2}x^2-\frac{1}{2}$$

$$P_3(x)=\frac{5}{2}x^3-\frac{3}{2}x$$

$$P_4(x)=\frac{35}{8}x^4-\frac{15}{4}x^2+\frac{3}{8}$$

$$\ldots \quad (14)$$

Polynomials of higher degree are determined by use of the recursion formula,

$$(m+1)P_{m+1}(x)+mP_{m-1}(x)-(2m+1)xP_m(x)=0. \quad (15)$$

The weight coefficients, H_m, can be determined from the roots, x_m,

$$H_m=\frac{2}{(1-x_m^2)[P'_m(x_m)]^2}. \quad (16)$$

Since the available weights, H_m, and abscissas, x_m, are limited [6], ($M=48$), it is quite possible for very precise work to split each integral somewhat arbitrarily but consistent with efficiency,

$$\int_{\Omega_a}^{\Omega_b} f(\Omega)d\Omega=\int_{\Omega_a}^{\Omega^{(1)}} f(\Omega)d\Omega+\int_{\Omega^{(1)}}^{\Omega^{(2)}} f(\Omega)d\Omega$$

$$+\int_{\Omega^{(2)}}^{\Omega^{(3)}} f(\Omega)d\Omega+\ \ldots\ +\int_{\Omega^{(n-1)}}^{\Omega_b} f(\Omega)d\Omega, \quad (17)$$

where $\Omega^{(n)}\equiv\Omega_b$, and a specified number of intervals, $n=1, 2, 3 \ . \ . \ .$, has been selected with limits of integration, Ω_a, $\Omega^{(1)}$, $\Omega^{(2)}$, $\Omega^{(3)}$, $\ldots \Omega_b$. Each integral is evaluated by the previously described quadrature (8, 9) with the abscissas and weights ($M=48$).

3. Computation

The first and second moment integrals, $\overline{[\Omega]}$ and $\sigma_\Omega{}^2$, were evaluated between the limits, $\Omega_a=0$, $\Omega_b=\pi$, employing the ($M=48$) Gaussian abscissas, x_m, and weights, H_m, for values of average relative intensity, k^2, between 0.01 and 1,000 of the random Rayleigh distributed component. According to the theory of Gaussian quadrature, this integration is equivalent to fitting a polynomial of degree $2m-1=95$ at 48 points, to the integrand, which points are weighted according to previously described rules (12) at the particular values of phase, $\Omega=\Omega_m(11)$.

The integration was checked at values, $k^2=0.01$, 0.1, 1, 10, 100 and 1,000, by splitting the integral into two integrals, $\Omega_a=0$, $\Omega_1=\frac{\pi}{2}$, $\Omega_b=\pi$, $n=2$, (17). The maximum difference between the value of either $\overline{[\Omega]}$ or σ_Ω obtained in this way (17) and that obtained with a single integral (9) was ± 1 in the eighth significant figure. There are indications that the last two significant figures could possible be in error in certain instances. This is probably due to the electronic data processing method [3] rather than the quadrature. The results of the computation are illustrated in figure 1 and are presented in table 1[4].

[3] I.B.M. 650–407–E.D.P. machine.

[4] The integer to the right of each table entry, if present, indicates the power of the factor of 10 by which the number is multiplied, thus positioning the decimal point. For example, 5.6513905 −2 means 0.056513905. Note that for $k^2=\infty$, $\sigma_\Omega=\pi/\sqrt{3}$ and $\overline{[\Omega]}=\pi/2$.

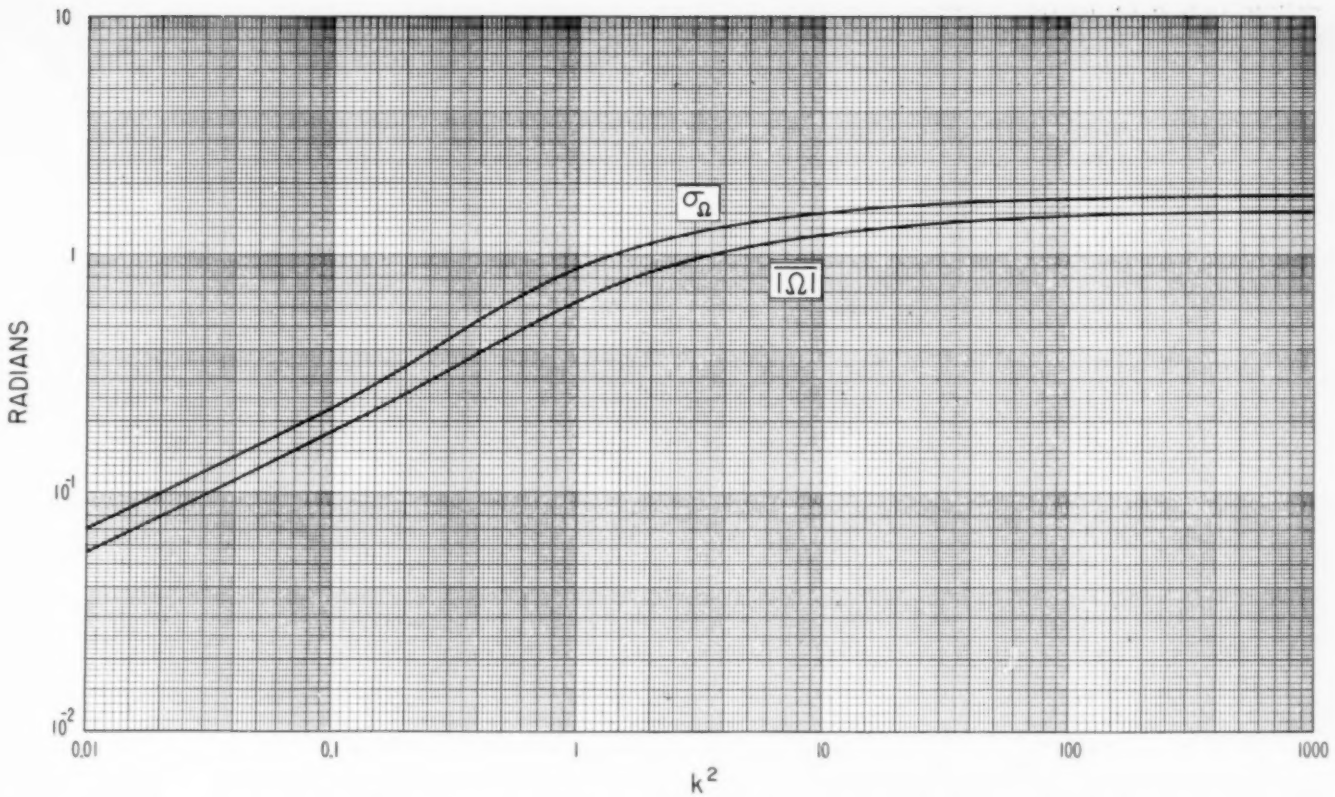

FIGURE 1. *Mean absolute value,* $\overline{|\Omega|}$, *and standard deviation,* σ_Ω, *as a function of the average relative intensity,* k^2, *of the random Rayleigh-distributed component.*

TABLE 1

k^2	$\overline{\Omega}$ radians	σ_Ω radians	k^2	$\overline{\Omega}$ radians	σ_Ω radians	k^2	$\overline{\Omega}$ radians	σ_Ω radians	k^2	$\overline{\Omega}$ radians	σ_Ω radians
0.010	5.6513905 −2	7.0889665 −2	0.090	1.7204794 −1	2.1758636 −1	0.80	5.7651767 −1	7.8540860 −1	7.0	1.1573886	1.4351373
.011	5.9281802 −2	7.4368405 −2	.091	1.7303579 −1	2.1886366 −1	.81	5.8018927 −1	7.9022010 −1	7.1	1.1601429	1.4378157
.012	6.1928049 −2	7.7695630 −2	.092	1.7401916 −1	2.2013540 −1	.82	5.8382359 −1	7.9497130 −1	7.2	1.1628333	1.4404390
.015	6.9273763 −2	8.6933250 −2	.095	1.7694134 −1	2.2391945 −1	.85	5.9450880 −1	8.0887390 −1	7.5	1.1705980	1.4479959
.020	8.0059192 −2	1.0051253 −1	.10	1.8172472 −1	2.3012770 −1	.90	6.1162274 −1	8.3093795 −1	8.0	1.1826098	1.4596450
.021	8.2050463 −2	1.0302171 −1	.11	1.9098601 −1	2.4221559 −1	.91	6.1494579 −1	8.3519350 −1	8.1	1.1848849	1.4618459
.022	8.3996053 −2	1.0547390 −1	.12	1.9992282 −1	2.5393404 −1	.92	6.1823668 −1	8.3939890 −1	8.2	1.1871207	1.4640069
.025	8.9586354 −2	1.1252438 −1	.15	2.2508374 −1	2.8749828 −1	.95	6.2792124 −1	8.5172250 −1	8.5	1.1936018	1.4702620
.030	9.8223130 −2	1.2342886 −1	.20	2.6328686 −1	3.4032320 −1	1.0	6.4346186 −1	8.7133750 −1	9.0	1.2037103	1.4799801
.031	9.9864106 −2	1.2550275 −1	.21	2.7053872 −1	3.5059207 −1	1.1	6.7247370 −1	9.0744135 −1	9.1	1.2056364	1.4818398
.032	1.0148000 −1	1.2754525 −1	.22	2.7767192 −1	3.6077869 −1	1.2	6.9802834 −1	9.3992080 −1	9.2	1.2075323	1.4836595
.035	1.0618661 −1	1.3349834 −1	.25	2.9848460 −1	3.9085106 −1	1.5	7.6682649 −1	1.0205470	9.5	1.2130479	1.4889462
.040	1.1361951 −1	1.4291103 −1	.30	3.3147043 −1	4.3923906 −1	2.0	8.5195625 −1	1.1175455	10	1.2217077	1.4972268
.041	1.1505149 −1	1.4472622 −1	.31	3.3783684 −1	4.4863226 −1	2.1	8.6599580 −1	1.1331300	11	1.2372944	1.5120705
.042	1.1646980 −1	1.4652086 −1	.32	3.4413045 −1	4.5792448 −1	2.2	8.7925345 −1	1.1477455	12	1.2509646	1.5250259
.045	1.2061991 −1	1.5179011 −1	.35	3.6258665 −1	4.8517326 −1	2.5	9.1498336 −1	1.1866651	15	1.2836835	1.5558026
.050	1.2726013 −1	1.6022582 −1	.40	3.9198002 −1	5.2841280 −1	3.0	9.6399295 −1	1.2389014	20	1.3212337	1.5907359
.051	1.2854991 −1	1.6186000 −1	.41	3.9767434 −1	5.3672815 −1	3.1	9.7254727 −1	1.2480052	21	1.3271198	1.5961754
.052	1.2982785 −1	1.6349168 −1	.42	4.0326502 −1	5.4493255 −1	3.2	9.8075157 −1	1.2566181	22	1.3326079	1.6012886
.055	1.3359414 −1	1.6828606 −1	.45	4.1978140 −1	5.6888385 −1	3.5	1.0034854	1.2803230	25	1.3470845	1.6145548
.060	1.3966386 −1	1.7602361 −1	.50	4.4604899 −1	6.0664350 −1	4.0	1.0361770	1.3140093	30	1.3662719	1.6321174
.061	1.4084930 −1	1.7753642 −1	.51	4.5112729 −1	6.1388105 −1	4.1	1.0420645	1.3200272	31	1.3695492	1.6351074
.062	1.4202581 −1	1.7903826 −1	.52	4.5614885 −1	6.2101680 −1	4.2	1.0477624	1.3258374	32	1.3726740	1.6379555
.065	1.4550327 −1	1.8348099 −1	.55	4.7088033 −1	6.4182710 −1	4.5	1.0638134	1.3421326	35	1.3812409	1.6457515
.070	1.5113924 −1	1.9069203 −1	.60	4.9436251 −1	6.7460915 −1	5.0	1.0875730	1.3660625	40	1.3933403	1.6567292
.071	1.5224405 −1	1.9210734 −1	.61	4.9880499 −1	6.8089385 −1	5.1	1.0919370	1.3704336	41	1.3954936	1.6586796
.072	1.5334169 −1	1.9351423 −1	.62	5.0339766 −1	6.8709150 −1	5.2	1.0961852	1.3746814	42	1.3975702	1.6605589
.075	1.5659419 −1	1.9768590 −1	.65	5.1658413 −1	7.0517715 −1	5.5	1.1082832	1.3867404	45	1.4033835	1.6658143
.080	1.6188698 −1	2.0448601 −1	.70	5.3763008 −1	7.3371715 −1	6.0	1.1265439	1.4048374	50	1.4118941	1.6734927
.081	1.6292752 −1	2.0582473 −1	.71	5.4170535 −1	7.3919745 −1	6.1	1.1299436	1.4081929	51	1.4134456	1.6748905
.082	1.6396238 −1	2.0715680 −1	.72	5.4573767 −1	7.4460535 −1	6.2	1.1332664	1.4114684	52	1.4149523	1.6762476
.085	1.6703356 −1	2.1111367 −1	.75	5.5758218 −1	7.6040620 −1	6.5	1.1428021	1.4208462	55	1.4192256	1.6800932

TABLE 1.—*Continued.*

k^2	$\overline{\Omega}$ radians	σ_Ω radians	k^2	$\overline{\Omega}$ radians	σ_Ω radians
60	1.4256277	1.6858461	400	1.5143646	1.7646036
61	1.4268134	1.6869104	410	1.5150558	1.7652101
62	1.4279704	1.6879488	420	1.5157220	1.7657947
65	1.4312811	1.6909181	450	1.5175857	1.7674297
70	1.4363217	1.6954337	500	1.5203113	1.7698191
71	1.4372656	1.6962787	510	1.5208079	1.7702541
72	1.4381902	1.6971060	520	1.5212898	1.7706766
75	1.4408523	1.6994873	550	1.5226565	1.7718738
80	1.4449535	1.7031527	600	1.5247021	1.7736652
81	1.4457283	1.7038446	610	1.5250810	1.7739967
82	1.4464888	1.7045237	620	1.5254503	1.7743202
85	1.4486897	1.7064882	650	1.5265072	1.7752451
90	1.4521112	1.7095402	700	1.5281154	1.7766522
91	1.4527618	1.7101201	710	1.5284164	1.7769155
92	1.4534017	1.7106904	720	1.5287113	1.7771734
95	1.4552605	1.7123466	750	1.5295601	1.7779157
100	1.4581716	1.7149389	800	1.5308671	1.7790585
110	1.4633887	1.7195798	810	1.5311138	1.7792741
120	1.4679420	1.7236250	820	1.5313563	1.7794859
150	1.4787613	1.7332182	850	1.5320572	1.7800987
200	1.4910552	1.7440872	900	1.5331466	1.7810506
210	1.4929717	1.7457784	910	1.5333538	1.7812315
220	1.4947562	1.7473525	920	1.5335573	1.7814094
250	1.4994527	1.7514919	950	1.5341489	1.7819263
300	1.5056546	1.7569509	1000	1.5350752	1.7827352
310	1.5067115	1.7578805			
320	1.5077186	1.7587659			
350	1.5104767	1.7611897			

4. Discussion and Conclusions

The problem formulated in this paper was the evaluation of two integrals—the first and second moments of the probability distribution of the phase of a constant vector plus a Rayleigh-distributed vector. These integrals were evaluated by an application of the theory of Gaussian quadrature and the results indicate that the method provides an efficient and precise solution to the problem.

It is quite possible to estimate the entire probability distribution from physical measurements of the standard deviation or the mean absolute value of the phase with the aid of the table or figure. This work therefore provides an analysis tool for the study of phase fluctuations in radio navigation and phase modulation systems.

This work was suggested by K. A. Norton and performed under National Bureau of Standards Project 8330–11–8332. The careful electronic computer work was developed by L. C. Walters.

5. References

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[4] Private communication.

[5] Z. Kopal, Numerical Analysis, p. 367 (John Wiley & Sons, Inc., New York, N. Y., 1955). See also p. 347.

[6] For tables of H_m and x_m see P. Davis and P. Rabinowitz, Abscissas and weights for Gaussian quadrature of high order, J. Research NBS **56,** 35 (1956) RP2645. (M= 64, 80, 96 are available although apparently unpublished.)

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Simple Rotating Molecular Still

Gaylon S. Ross and Lois J. Frolen

A simple molecular still has been designed to purify materials which have a low vapor pressure and which are thermally unstable. The apparatus contains no ground glass joints and the distillation is accomplished in a completely closed system. The efficiency of the still was found to be better than that for either the pot-type or the falling film-type molecular stills generally used.

In recent years a number of rotating evaporators and molecular stills that employ a mobile thin film have been developed. The rotating evaporators which have been described are unsatisfactory as molecular stills because: (1) The joints which are required either leak, or if lubricated, may contaminate the sample; and (2) they are not readily adaptable to multiple stages. The mobile film molecular stills, while satisfying these objections are quite complex and even more expensive than the evaporators.

The apparatus was designed to purify materials which have a low vapor pressure and which are thermally unstable at elevated temperatures. The apparatus is simple and inexpensive. After the glass assembly is made, all other components are usually available in the laboratory. It is free of all ground glass joints, can be extended to as many stages as desired, and can be designed to remove several fractions by collecting in more than 1 ampoule. The essential features of the apparatus are shown in figure 1.

The method used is as follows: The sample is poured into bulb A while the unique axis of the apparatus is in a vertical position with bulb A on the bottom. The entrance tube C is then sealed to a vacuum line, and the sample is degassed by alternately freezing and melting under continuous pumping. When the degassing is completed, tube C is flame-sealed, and the apparatus is mounted in a nearly horizontal position on a rack as shown in figure 1. Two band clamps, D and J, beside the protruding rings, E and I, serve as supports and bearings for the apparatus. A rubber O-ring is mounted at H and connected to the drive wheel of a motor which rotates the entire apparatus at 1 to 2 rpm. A wide-mouthed Dewar flask containing liquid nitrogen or a slush of solid carbon dioxide in a suitable liquid is placed under the collecting bulb F and an infrared lamp is placed several inches above bulb A. The lamp heats the thin film of liquid on the surface of the bulb. This has the advantages that the surface film of the sample is continually renewed and that the bulk of the liquid remains cool, thereby limiting thermal decomposition. The process is repeated by placing the Dewar flask with cooling bath under bulb K and the lamp above bulb F. When the second stage of the process is completed, the entire apparatus is clamped in the inverted vertical position with ampoule M on the bottom. The frozen sample in bulb K is allowed to melt and flow into the breakoff tip, ampoule M. The residue in A and F is retained during this pouring process by the protruding ring seals at B and G. The sample is then frozen and the ampoule is flame-sealed at L.

This apparatus is 5 to 100 times as rapid as the usual pot-type molecular still. The rate can be controlled by adjusting the pressure in the system or by raising or lowering the heat source. Under normal operation the main body of the distilling sample is only a few degrees above room temperature. If necessary, the film can be made much hotter by lowering the lamp, while at the same time the bulk of the liquid is maintained at or below room temperature by supplementary cooling. The efficiency of the apparatus, as shown by the removal of colored bodies, was higher than either the pot or falling-film type of molecular stills generally used.

The method has been used to remove colored impurities and higher molecular-weight oxidation products from fluoro-, chloro-, bromo-, iodo-, methyl-, t-butyl-, and unsubstituted dimethylanilines and the analogous anisoles. Also the purification of high-boiling residues from crude ethyldichlorobenzene stocks has been successfully achieved by using this technique. With the pot-type still this same material could not be distilled.

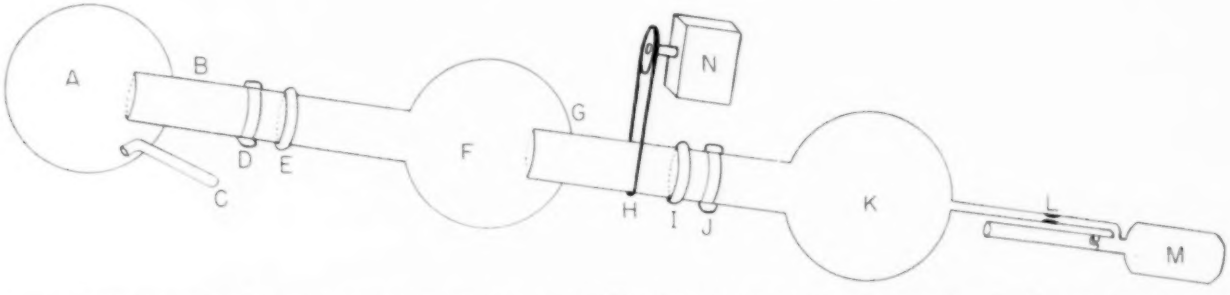

FIGURE 1. *Rotating molecular still, operating position A, F, K, 500 ml bulbs; C, entrance tube; B, G, annular rings; D, J, band clamps used as bearings; E, I, alining protrusions; H, rubber O-ring; L, sealing constriction; M, ampoule; N, motor; axis inclined at about 10° in respect to the horizon.*

WASHINGTON, December 8, 1958.

Journal of Research of the National Bureau of Standards Vol. 62, No. 5, May 1959 Research Paper 2952

Scintillation Counter Method of Intercomparing Neutron Source Strengths by Means of a Manganous Sulfate Bath

Earl R. Mosburg, Jr.

It has proved feasible to use a scintillation counter to measure the relative activity of a large manganous sulfate bath, thereby determining the neutron-emission rates of neutron sources relative to the national standard neutron source of the National Bureau of Standards. A scintillation counter allows the calibration of sources weaker by a factor of seven than those it was previously possible to calibrate by means of a Geiger-Muller counter. The use of Cs^{137} as a reference pulse height to which the scintillation counter system is adjusted by means of a two channel pulse height analyzer makes possible the reliable reproduction of results from day to day. By using the scintillation counter the ratio of the national reference standard neutron source (NBS–II) to the national standard neutron source (NBS–I) has been redetermined and is found to be $0.939_3 \pm 0.001_7$.

1. Introduction

The routine determination of neutron-emission rates of "radioactive" neutron sources in terms of the emission rate of the NBS Ra-Be (γ,n) national standard source, known as NBS–I, has for sometime been carried out by means of a manganous sulfate bath. In this method, which was also used to calibrate the national neutron standard absolutely,[1] the source is suspended for approximately 18 hr in the center of a cylindrical bath of manganous sulfate solution of 1-m depth and 1-m diam. The fast neutrons are moderated in the water and an appreciable and constant fraction of them are then captured by the manganese. Integration of the Mn^{56} activity over all radii is accomplished by thoroughly mixing the solution before the count is started. Counting of the Mn^{56} activity has normally been accomplished by the use of a Geiger-Muller counter suspended in the center of the bath. This paper will describe the use of a scintillation counter placed in the center of the bath and the means used to obtain the high degree of pulse-height reproducibility and stability that is required.

When the bath is activated to near saturation by NBS–I (neutron yield $Q=1.26\times10^6$ neutrons/sec) and counted with a Geiger counter,[2] the integrated count over approximately a half life of Mn^{56} (2.58 hr) is 31,300 counts, of which 12 percent are due to background radiation. Assuming an equal counting time in determining the background, the statistical error $(\sqrt{n})$, in the value of the bath activity is then close to 0.7 percent. Background levels show slight changes over periods of days which further add to this uncertainty. If a calibration of a weaker source is desired, the accuracy quickly worsens. For example, if the neutron yield of the source is 10^5 neutrons/sec the background amounts to 62 percent of the total count and the statistical error in the value of the bath activity is 4.4 percent.

To obtain ratios of the neutron yields of two sources to accuracies of 0.5 percent, some improvement in the calibration procedure is indicated. An increase in counting time is of no avail since we already have half of the total time integrated count obtainable with the Geiger counter system.

2. Scintillation Counter Method

A much higher efficiency is achieved if, instead of a Geiger counter, a NaI(Tl) scintillator is used for dip counting of the activated manganese. However, a scintillation counter produces a continuous pulse height distribution with a general increase in the number of pulses at lower pulse heights until the distribution blends into the noise spectrum of the photomultiplier tube. Thus some discrimination level must be set and pulses of height lower than this limit rejected. This discrimination level must be capable of accurate repetition from day to day and must possess considerable time stability. The overall gain stability of the system must be appreciably better than one percent. In addition it must be possible to determine the position of the discrimination level by a means which will give accuracies of better than 1 percent within a short period of time.

The use of the sharp 662 Kev γ-line of Cs^{137} offers a quick and accurate pulse height reference. As is shown in the block diagram (fig. 1) the Cs^{137} pulses from the probe, after amplification in a linear amplifier, are fed to a two-channel differential pulse height analyzer consisting of a triple discriminator of high stability followed by a dual-channel anticoincidence circuit. The spacing between the levels of the triple discriminator is fixed at about half of the width of the cesium peak. The calibration of the pulse height is then made by adjusting the gain of the amplifier for equal counting rates in the two pulse-height channels when the cesium source is near the probe. In

[1] James DeJuren and Jack Chin, J. Research NBS **55**, 311 (1955) RP2635.

[2] N. Wood Counter Laboratory, Chicago, Ill., 4½ in. active length, 1 in. diameter.

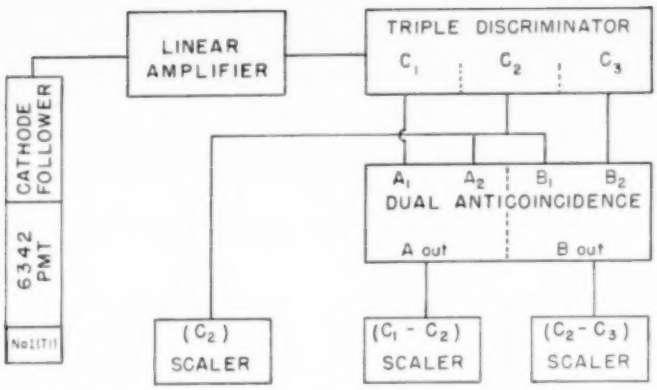

FIGURE 1. *Block diagram of electronic circuitry.*

figure 2 are shown the pulse-height distributions obtained from Cs^{137} and Mn^{56} as well as the positions of the triple discriminator levels, C_1, C_2, and C_3. After the pulse-height adjustment with the cesium, the cesium source is removed and the bath activity is determined by counting the output C_2 of the triple discriminator which is then centered on the cesium peak. Considering small variations in amplification, it is clear that a relatively small percentage change in the count rate of discriminator C_2 for a cesium source is associated with a much smaller percentage change for a Mn^{56} source. The ratio is in fact about 16. The statistical error in the count rate difference between the two pulse height channels for a 1-min count with the cesium source in the standard position permits an accuracy in the adjustment of pulse height which corresponds to an error of only 0.04 percent in the Mn^{56} count rate. There are still present, however, short term variations in the overall gain which cause the difference in the count rates of the two channels to vary, during a period of an hour or less, by an amount greater than the statistical error associated with a 1-min cesium count. These variations, which correspond to pulse height variations of less than 0.4 percent, are associated with less than a 3.5-percent error in the cesium count rate or less than a 0.2-percent error in the Mn^{56} count rate.

The use of a $1\frac{1}{2} \times 1\frac{1}{2}$ in. NaI(Tl) scintillation counter in determining bath activity provides counting rates which are higher by a factor of 9 than those of the Geiger counter previously used. Moreover, the fact that the percentage of pulses which are of pulse height above the discrimination level is lower for the background than for Mn^{56}, results in a reduction in the ratio of background to total count from 12 percent to 3 percent when the bath is activated by NBS–I. Thus sources of lower total neutron yield may now be calibrated in the bath. Table 1 compares the statistical errors in the determination of bath activity for sources of various neutron yields by both the Geiger and scintillation counter methods. If the statistical error in the determination of the bath activity is required to be less than 1.0 percent the use of the scintillation counter allows the calibration of a source smaller in yield by a factor of more

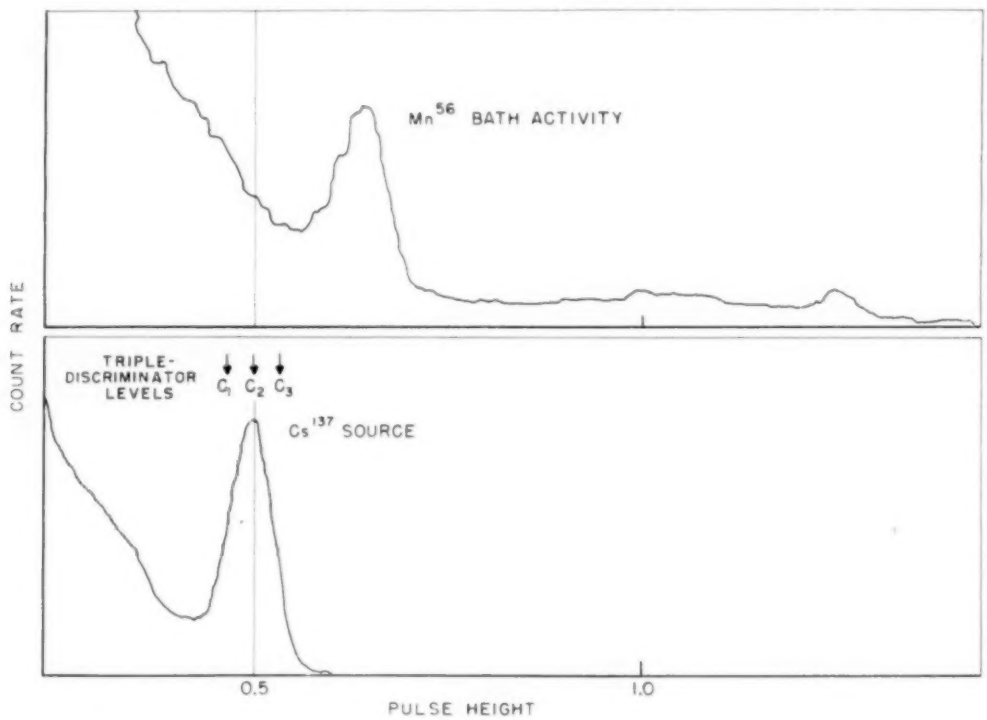

FIGURE 2. *Pulse height distributions from gamma rays from* Mn^{56} *in manganous sulfate bath and from* Cs^{137} *source.*

TABLE 1. *Calculated values associated with the measurement of the manganous sulfate bath activity*

Neutron emission rate of the source	Geiger counter 155-min count		Scintillation counter 155-min count		Scintillation counter 15-min count	
	Ratio of background to total	Standard deviation in bath activity[a]	Ratio of background to total	Standard deviation in bath activity[a]	Ratio of background to total	Standard deviation in bath activity[a]
		%		%		%
1.26×10^6 (NBS–I)	0.116	0.68	0.029	0.21	0.029	0.66
7×10^5	.193	.98	-----	-----	-----	-----
3×10^5	.36	1.8	.111	0.49	-----	-----
10^5	.62	4.4	.273	0.94	-----	-----

[a] In computing the standard deviation, the background count is assumed equal in length to the activated bath count in each case.

than seven or the calibration of a source of yield 1.26×10^6 in less than one-tenth of the time required by the Geiger counter. Of course these values apply only to the specific counter used. Improvements in sensitivity can easily be made by simply using a larger scintillator in the bath.

In order to achieve the needed stability in gain, the scintillator and photomultiplier must be temperature stabilized. The pulse height from such scintillating systems has a negative temperature coefficient which amounts to as much as 0.5 percent per degree centigrade.[3] The temperature stabilization is accomplished by immersing the probe in the manganous sulfate bath one-half hour before adjusting the gain on the cesium peak. The heat capacity of the bath is sufficiently large to preclude any appreciable temperature change over the combined time interval required for the gain adjustment with cesium and for the subsequent count of the bath activity.

Another effect which was considered is the variation of pulse height with counting rate.[4] The change in pulse height with count rate was determined by observing the shift in the balance point with the Cs^{137} source in a standard position, when a Ba^{133} source was placed at various distances from the source. The spectrum of the Ba source has a maximum pulse height below the cesium peak and thus does not contribute counts in the region of the cesium peak. The absolute count rate in the photomultiplier tube due to the cesium source was estimated using an extrapolation of the cesium pulse height distribution to zero pulse height. The absolute count rates with both cesium and Ba^{133} present were then estimated by relative measurements with the scintillation counter replaced by a Geiger counter. A variation of count rate by a factor of two from that due to the cesium source alone results in a shift in pulse height of the cesium peak of about 0.25 percent. This would correspond to an error in the manganese bath count of 0.13 percent. Since most of the sources tested are of approximately the same strength this factor is not too important. However this effect will be investigated more thoroughly.

[3] W. P. Ball, R. Booth, and M. MacGregor, Nuclear Instruments **1**, 71 (1957).
[4] P. R. Bell, R. C. Davis, and W. Bernstein, Rev. Sci. Instr. **26**, 726 (1955).

3. Redetermination of the Ratio of NBS Standard Sources

The ratio of the emission rate (Q) of the National Bureau of Standards national reference standard neutron source NBS–II to that of the national neutron standard NBS–I was redetermined using the scintillation dipcounter in a series of measurements involving five irradiations of the bath by NBS–I and four by NBS–II. The best value for the ratio, based on 21 counts of the NBS–I bath activity and 16 counts of the NBS–II bath activity, is:

$$\frac{Q(\text{NBS–II})}{Q(\text{NBS–I})}=0.939_3\pm0.001_7$$

where the error given is the standard deviation, which is about 30 percent higher than the error expected on the basis of $\sqrt{n}$ alone. The distributions of deviations from the weighted average values of the bath activities are normal and the largest deviation for a single measurement is about $3\frac{1}{2}$ standard deviations.

The author thanks Louis Costrell for the design of some of the circuits and William Murphy and Jack Chin for assistance in taking the data.

WASHINGTON, December 29, 1958.

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Phase Equilibria in the Subsystem Barium Disilicate—Dibarium Trisilicate

Robert S. Roth and Ernest M. Levin

A revised phase equilibrium diagram for the subsystem $BaO{\cdot}2SiO_2$—$2BaO{\cdot}3SiO_2$ is presented. The previously published diagram showing a complete solid solution series was not verified. Instead, two new compounds were identified by X-ray diffraction powder pattern techniques, and two eutectics were located by the quenching method. The compound $3BaO{\cdot}5SiO_2$ melts incongruently at 1,423° C to form $5BaO{\cdot}8SiO_2$ and liquid. The latter compound melts congruently at 1,446° C. Barium disilicate was found to have a quenchable and slowly reversible phase transformation at about 1,350° C. The X-ray diffraction powder pattern for $2BaO{\cdot}3SiO_2$ was indexed for the first time on the basis of a monoclinic unit cell.

1. Introduction

In a study of the phase equilibria of the binary system BaO-SiO_2, P. Eskola [1] [1] confirmed the existence of barium disilicate, previously reported by Bowen [2]. The phase diagram published by Eskola showed complete solid solution between $BaO{\cdot}2SiO_2$ and $2BaO{\cdot}3SiO_2$. Rogers [3] discovered the existence of barium disilicate in nature and gave it the mineral name of sanbornite. In order to reconcile his findings with those of Bowen and Eskola, Rogers postulated dimorphism in $BaSi_2O_5$, indicating that sanbornite was probably triclinic, whereas the synthetic material was apparently orthorhombic. In a study of the BaO-Al_2O_3-SiO_2 system, R. H. Thomas [4] concluded that dibarium trisilicate probably was not a compound, but rather a fortuitous end-member of a solid solution series.

Levin and Ugrinic [5] and Toropov, Galakhov, and Bondar [6] concluded that dibarium trisilicate most likely was a true compound and that complete solid solution existed between it and barium disilicate. Levin and Ugrinic, nevertheless, state, "The X-ray data, however, did not conclusively show a solid solution series. The powder pattern for the composition containing 70.8 percent $BaO{\cdot}2SiO_2$ (29.2 percent of $2BaO{\cdot}3SiO_2$) showed several double peaks which indicated the presence of two phases. Even after an additional melting and grinding of the mixture, these double peaks persisted."

R. M. Douglass [7] recently reported the crystal structure of the mineral sanbornite. The unit cell was found to be orthorhombic with $a=4.63$ A, $b=8.69$ A, and $c=13.53$ A. Douglass concluded that barium disilicate did not show polymorphism although his X-ray diffraction powder pattern did not match that of Levin and Ugrinic [5].

On the basis of the structure determined for sanbornite, Douglass [7] doubted that extensive solid solution existed between barium disilicate and dibarium trisilicate.

The opinions expressed by Douglass led to a reexamination of the possibilities of polymorphism in barium disilicate. Unpublished high-temperature X-ray patterns prepared during the original investigation of Levin and Ugrinic [5] had not been interpreted as showing conclusive evidence of polymorphism. However, with the ability to index the low-temperature form, as a result of Douglass' work, polymorphic transformation was clearly indicated in these patterns. In a note preliminary to this publication [8] polymorphism in barium disilicate was announced. The complete data supporting that statement are presented in this paper. In an attempt, also, to resolve the controversial question of solid solution in barium disilicate, a detailed reexamination is reported for the subsystem $BaO{\cdot}2SiO_2$-$2BaO{\cdot}3SiO_2$.

2. Apparatus and Method

Phase equilibrium relationships in the system were studied by the well-established quenching technique. It was found that all liquids could be readily quenched to glasses. Constant temperature control of the quench furnace to within $\pm 3°$ C was achieved with a self-adjusting, a-c bridge-type controller [9]. Quenched samples were examined with the polarizing microscope and by X-ray powder diffraction patterns (Ni-filtered CuK radiation) using a high-angle Geiger-counter diffractometer.

Temperatures were measured with a platinum versus platinum-rhodium (10%) thermocouple which was taken from lengths of thermocouple wire which had been originally calibrated by the Pyrometry Laboratory. Temperatures are given on the International Temperature Scale of 1948. During the course of the experiments the thermocouple was checked three times against the melting point of barium disilicate (1,420° C).

[1] Figures in brackets indicate the literature references at the end of this paper.

3. Preparation of Mixtures

Starting materials for the preparation of mixtures consisted of reagent grade (ACS) barium carbonate and silica gel of 99.99-percent purity on an ignited weight basis. The silica gel was specially prepared by an acid digestion process in the Chemistry Division.

The end-members $BaO{\cdot}2SiO_2$ and $2BaO{\cdot}3SiO_2$ as well as the composition containing 37.4-mole percent BaO were specimens used in a previous study [5], and their preparation was described therein. Six intervening mixtures with BaO contents ranging from 34- to 39-mole percent, in 1-mole-percent increments, were prepared as follows: Calculated amounts, for 3–g mixtures, of barium carbonate and silica gel were thoroughly blended for ½ hr with a high-speed mechanical mixer. The mixtures were then ground for ½ to ¾ hr in an agate mechanical grinder. Specimens, ⅝ in. in diameter, were formed by pressing the material in a mold at approximately 20,000 psi. The pressed disks were fired in a pot furnace at about 1,300° C for 24 hr. The disks were ground through a No. 200 sieve, pressed as before, and given a second heat treatment at 1,375° ±15° C for 84 hr. Finally, the disks were ground to pass a No. 200 sieve. The two relatively long-time, high-temperature, heat treatments of pressed specimens were sufficient, apparently, to give homogeneous samples, as determined by inspection with the polarizing microscope.

For locating compounds and eutectics, 5 additional l-g samples were prepared from the appropriate amounts of previously prepared adjacent samples. The method of combination was similar to that for the 3–g samples.

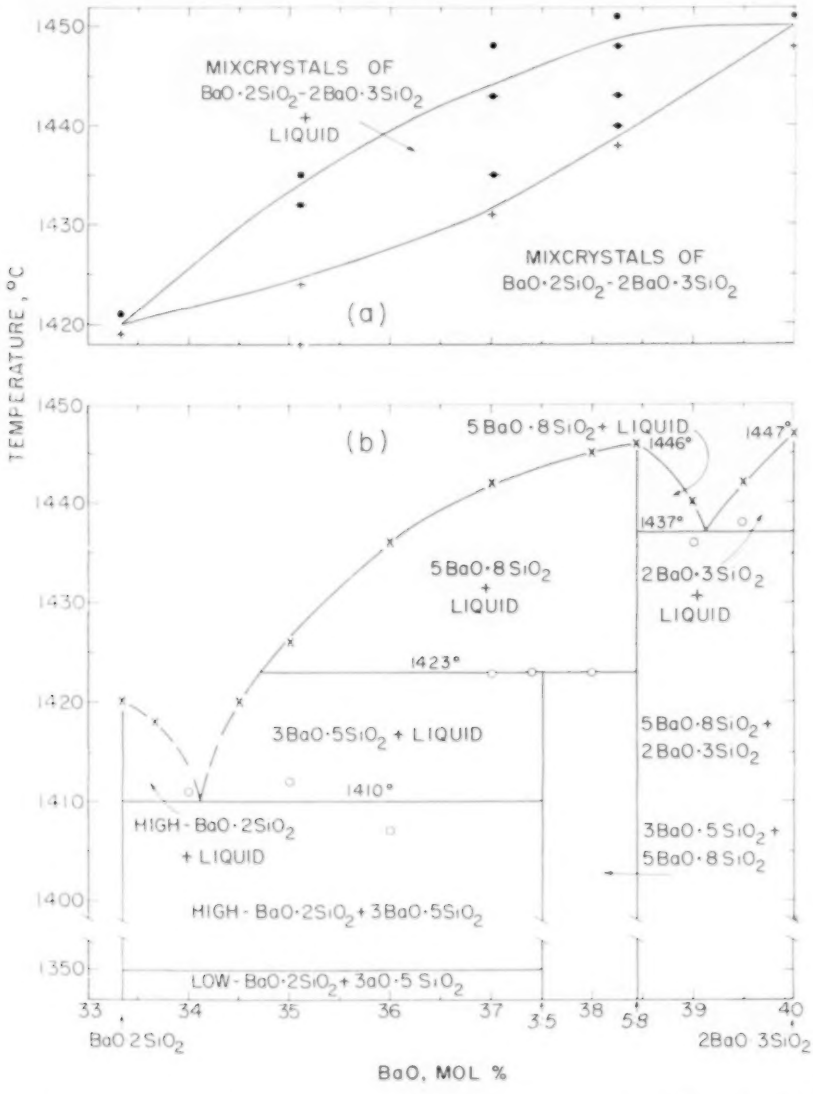

FIGURE 1. *Phase equilibrium diagrams proposed for the subsystem* $BaO{\cdot}2SiO_2$—$2BaO{\cdot}3SiO_2$.

(a) Continuous solid solution diagram according to Eskola [1], with data converted to mole percent. ●, glass; —●— mixcrystals and glass; +, mixcrystals.
(b) Diagram without solid solution, according to the present work, showing two compounds and two eutectics. ×, liquidus value; O, solidus value.

4. Results and Discussion

The results of the experiments in the system $BaO{\cdot}2SiO_2$-$2BaO{\cdot}3SiO_2$ are listed in table 1 for the 14 different compositions studied. These results have been interpreted to give the phase diagram shown in figure 1. Identification of crystalline phases by the polarizing microscope is given in the table only for those cases in which X-ray identification was not possible, because of a large proportion of glass. Because of overlapping indices of refraction, accurate identification of the crystalline phases present was difficult or impossible for many of the specimens. However, maximum and minimum indices usually were determined, and they were found to be compatible with the X-ray data.

4.1. Polymorphism of Barium Disilicate

Results of the experiments listed in table 1 for the 2 specimens containing 33.33-mole-percent BaO prove the existence of polymorphism in $BaSi_2O_5$. The heat treatment used to prepare the first composition listed in table 1 yielded the low-temperature form of $BaO{\cdot}2SiO_2$, or sanbornite. It may be seen that the low-temperature form remains stable at temperatures below 1,340° C. At temperatures of 1,352° C and above, however, the high-temperature form appears, in amounts which increase with the time and temperature of heat treatment. For example, the sample heated at 1,360° C for 1.5 hr failed to produce any detectable amounts of the high-temperature form, whereas the sample heated at 1,358° C for 16 hr showed appreciable conversion.

High-temperature X-ray diffraction patterns of the original low-temperature form were available from a previous study [5]. Upon re-examination the following features were observed: Except for slight shifts in interplanar spacings due to thermal expansion, no change was observed up to 1,300° C. After several hours at 1,375° C. notable differences were apparent in the diffraction pattern. The X-ray pattern of the sample, furnace-cooled to room temperature, still showed the high form of barium disilicate.

The second composition listed in table 1 was not initially heat treated below 1,390° C. It showed the pure high-temperature form. When it was heated at 1,335° C for 18 hr, the low-temperature form appeared in abundance. Interpretation of these data leads to the conclusion that barium disilicate exhibits a slowly reversible polymorphic transformation at 1,350° C ±10° C.

Figure 2 shows schematically the X-ray diffraction powder patterns of the 2 polymorphs compared with the patterns reported by Austin [10] and Douglass [7] for $BaO{\cdot}2SiO_2$. It is obvious from this figure that sanbornite (Douglass [7]) is identical with the low-temperature form of $BaO{\cdot}2SiO_2$, found in the present work. Austin's data appear to represent, at least in part, a poorly resolved pattern for high $BaO{\cdot}2SiO_2$.

The X-ray diffraction powder pattern for high-temperature $BaO \cdot 2SiO_2$ obtained in the present study is compared in table 2 with the pattern published by Levin and Ugrinic [5]. The present pattern is probably more accurate as it seems likely that the X-ray diffraction equipment used for the earlier work was out of alinement. The final accuracy of the d values must await indexing of the pattern following a determination of the unit-cell parameters.

The X-ray diffraction powder patterns of the 2 polymorphs are superficially simiar in that many of the strong lines of both patterns almost coincide. However, when an attempt is made to index the pattern of the high-temperature form, it is found that many of the interplanar spacings cannot be assigned indices on the basis of a structure resembling sanbornite. The diffraction peak at $2\theta = 25.1°$ or $d = 3.54$ A, is diagnostic of the high-temperature form. A number of other peaks cannot be reconciled with the sanbornite structure, as, for example, those at approximately 16° and 19° and the triplet at 28.5° 2θ (see fig. 2). It may be concluded that Douglass'

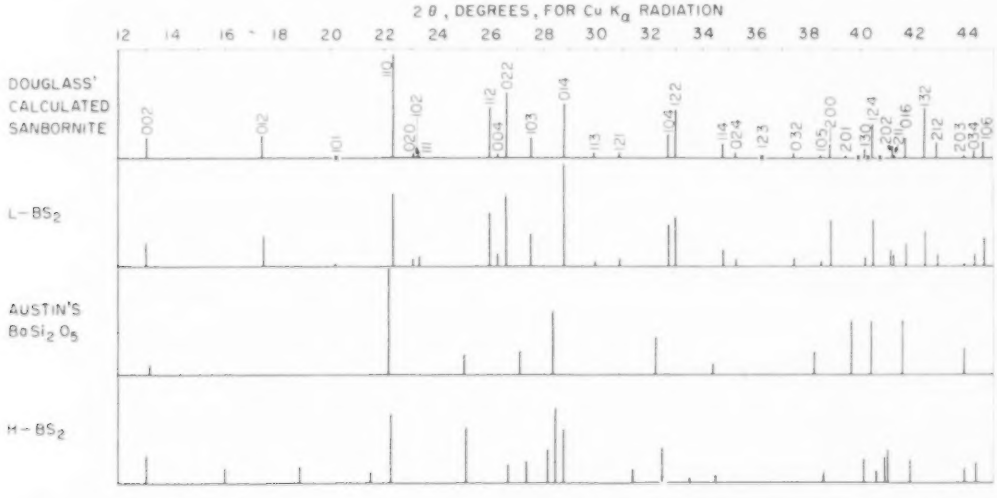

FIGURE 2. *Schematic X-ray diffraction powder patterns for the polymorphs of* $BaO{\cdot}2SiO_2$ *compared with two previously published patterns [7, 10].*

pattern is different from those reported by any of the authors mentioned in his paper [7]. Although Douglass correlated his pattern with Austin's published data, the present work proves that this correlation is incorrect. Austin's data should actually be correlated with the high-temperature form, as was done originally by Levin and Ugrinic [5].

4.2. Compound $2BaO \cdot 3SiO_2$

In order to obtain sufficient data to index the powder pattern, single crystals of $2BaO.3SiO_2$ were grown by A. Perloff of the Bureau on a hot-wire apparatus [11]. Precession patterns established the symmetry of the crystal as monoclinic, probably space group $C_2^2-P2_1$ or $C_{2h}^2-P2_{1/m}$. Using the approximate cell dimensions provided by Perloff, the X-ray diffraction powder pattern was indexed (table 3). The unit-cell parameters calculated from the powder pattern are: $a=12.51$ A; $b=4.69$ A; $c=6.97$ A; and $\beta=93°23'$.

Specimens of the composition containing 40-mole-percent BaO heated at 1,400° C for 3 hr or at 1,442° C for 0.5 hr (table 1) showed the same phase, namely, that present in the original starting material and in the crystals grown from the melt. The *d* values for this phase did not change regardless of composition or time and temperature of treatment. Consequently, within the limits of the present experiments, dibarium tricilicate shows neither polymorphism nor solid solution. The liquidus temperature of $2BaO \cdot 3SiO_2$ was determined to be 1,447° C, or about 3° less than that reported by Eskola.

4.3. Phase Diagram for the System $BaO \cdot 2SiO_2$—$2BaO \cdot 3SiO_2$

The phase diagram as reported by Eskola [1] (Fig. 1a) shows a continuous solid solution between $BaO \cdot 2SiO_2$ and $2BaO \cdot 3SiO_2$, without maximum or minimum. It should be noted that this diagram is based on only 3 intermediate compositions.

TABLE 1. *Compositions studied and phases identified in the system* $BaO \cdot 2SiO_2$-$2BaO \cdot 3SiO_2$

Composition		Heat treatment [a]		Phases		
BaO	SiO_2	Temperature	Time	X-ray diffraction [b]	Polarizing microscope	
					Crystals [c]	Amt. glass
mole %	*mole %*	*° C*	*hr*			
33.33	66.67	[d,e] 1,200	2.0	Low-$BaO \cdot 2SiO_2$		
($BaO \cdot 2SiO_2$)		1,340	52.0	---do		
		1,352	5.0	Low- +high-$BaO \cdot 2SiO_2$		
		1,358	16.0	---do		
		1,360	1.5	Low-$BaO \cdot 2SiO_2$		
		1,373	16.0	High- +low-$BaO \cdot 2SiO_2$		
		1,385	2.5	---do		
33.33	66.67	[d,f] 1,390	1.75	High-$BaO \cdot 2SiO_2$		
		1,335	18.0	Low- +high-$BaO \cdot 2SiO_2$		
		1,419	0.33	High-$BaO \cdot 2SiO_2$		
[e] 33.67	66.33	1,388	16.0	High- +low-$BaO \cdot 2SiO_2$+$3BaO \cdot 5SiO_2$		None.
		1,415	1.0	High-$BaO \cdot 2SiO_2$		Moderate.
		1,418	1.0		$BaO \cdot 2SiO_2$	Large.
34.00	66.00	[d,b] 1,375	84.0	High-$BaO \cdot 2SiO_2$+$3BaO \cdot 5SiO_2$		
		1,407	1.0	---do		None.
		1,414	1.0	High-$BaO \cdot 2SiO_2$[i]+$3BaO \cdot 5SiO_2$[i]		Small.
		1,417	3.0	---do		Moderate.
		1,420	0.5		$3BaO \cdot 5SiO_2$[i]+ $BaO \cdot 2SiO_2$.	Large.
		1,424	.5			All.
[j] 34.50	65.50	1,395	16.0	High-$BaO \cdot 2SiO_2$+$3BaO \cdot 5SiO_2$		None.
		1,415	0.5	$3BaO \cdot 5SiO_2$		Large.
		1,418	1.0		Trace	Do.
		1,421	1.0			All.
35.00	65.00	[d,b] 1,375	84.0	High-$BaO \cdot 2SiO_2$+$3BaO \cdot 5SiO_2$		None.
		1,410	1.0	---do		Do.
		1,416	1.0	$3BaO \cdot 5SiO_2$		Moderate.
		1,419	0.5		$3BaO \cdot 5SiO_2$	Large.
		1,423	.5		---do	Do.
		1,429	.5			All.
36.00	64.00	[d,b] 1,375	84.0	$3BaO \cdot 5SiO_2$+high-$BaO \cdot 2SiO_2$		
		1,340	16.0	$3BaO \cdot 5SiO_2$+high-[i]+low-$BaO \cdot 2SiO_2$		
		1,404	1.0	$3BaO \cdot 5SiO_2$+high-$BaO \cdot 2SiO_2$		None.
		1,410	1.0	$3BaO \cdot 5SiO_2$		Small.
		1,416	1.0	---do		Moderate.
		1,434	0.75		$3BaO \cdot 5SiO_2$[i]	Large.
		1,438	.5			All.
37.00	63.00	[d,b] 1,375	84.0	$3BaO \cdot 5SiO_2$+high-$BaO \cdot 2SiO_2$		
		1,411	1.0	$3BaO \cdot 5SiO_2$		None.
		1,419	1.0	---do		Trace.
		1,423	1.0	$3BaO \cdot 5SiO_2$+$5BaO \cdot 8SiO_2$ (tr)		Do.
		1,426	0.75	$3BaO \cdot 5SiO_2$[i]+$5BaO \cdot 8SiO_2$		Small.
		1,431	1.25	$5BaO \cdot 8SiO_2$		Moderate.
		1,440	0.5		Trace	Large.
		1,445	.75			All.

See footnotes at end of table.

TABLE 1. *Compositions studied and phases identified in the system* $BaO \cdot 2SiO_2$-$2BaO \cdot 3SiO_2$—Continued

Composition		Heat treatment [a]		Phases		
					Polarizing microscope	
BaO	SiO_2	Temperature	Time	X-ray diffraction [b]	Crystals [c]	Amt. glass
mole %	*mole %*	*° C*	*hr*			
37.41	62.59	[d f] 1,390	1.75	$3BaO \cdot 5SiO_2$		
		1,415	0.75			None.
		1,423	1.0	$5BaO \cdot 8SiO_2 + 3BaO \cdot 5SiO_2$		Trace.
		1,426	0.75	$5BaO \cdot 8SiO_2 + 3BaO \cdot 5SiO_2$ [i]		Small.
[k] 37.50 ($3BaO \cdot 5SiO_2$)	62.50	1,388	16.0	$3BaO \cdot 5SiO_2$		
		1,437	1.0	$5BaO \cdot 8SiO_2$		Small.
		1,440	1.0	do		Moderate.
38.00	62.00	[d h] 1,375	84.0	$5BaO \cdot 8SiO_2 + 3BaO \cdot 5SiO_2$		None.
		1,405	2.0	do		Do.
		1,415	1.25	do		Do.
		1,423	1.0	$5BaO \cdot 8SiO_2$		Trace.
		1,432	1.25	do		Small.
		1,441	1.25	do		Moderate.
		1,443	0.75		$5BaO \cdot 8SiO_2$	Large.
		1,447	1.00			All.
[l] 38.46 ($5BaO \cdot 8SiO_2$)	61.54	1,388	16.0	do		
		1,440	1.0	do		None.
		1,444	1.0		$5BaO \cdot 8SiO_2$	Large.
		1,447	1.0			All.
39.00	61.00	[d h] 1,375	84.0	$5BaO \cdot 8SiO_2 + 2BaO \cdot 3SiO_2$		
		1,405	2.0	do		None.
		1,425	1.0	do		Do.
		1,433	1.0	do		Do.
		1,438	0.8	$5BaO \cdot 8SiO_2$		Large.
		1,442	1.0			All.
[m] 39.50	60.50	1,388	16.0	$2BaO \cdot 3SiO_2 + 5BaO \cdot 8SiO_2$		
		1,437	1.0	do		None.
		1,440	1.0	$2BaO \cdot 3SiO_2 + 5BaO \cdot 8SiO_2$ (tr) [i]		Moderate.
		1,444	1.0			All.
40.00 ($2BaO \cdot 3SiO_2$)	60.00	[d e] 1,200	20.0	$2BaO \cdot 3SiO_2$		
		1,400	3.0	do		
		1,442	0.5		$2BaO \cdot 3SiO_2$	None.
		1,445	.5		do	Trace.
		1,450	1.5			All.

[a] Except where noted, all specimens were quenched in water, from the temperature indicated.
[b] Listed in order of relative amounts present, major phase first.
[c] Listed only when no X-ray identification was available.
[d] Starting material; not quenched.
[e] Sample previously heated at 1,460° C for ¾ hr, 1,100° C for 17 hr, and 1,400° C for 1 hr.
[f] Sample previously heated at 1,460° C for 1.5 hr, 1,390° C for 1 hr, 1,450° C for 1 hr.
[g] Prepared by mixing the appropriate amounts of the compositions low-$BaO \cdot 2SiO_2$ and 34.00 BaO:66.00 SiO_2.
[h] Sample previously heated at 1,300° C for 24 hr, 1,375° C for 3.5 hr, 1,360° C for 15.5 hr.
[i] Interpreted as non-equilibrium phase at the temperature indicated.
[j] Prepared by mixing the appropriate amounts of the compositions 34.00 BaO:66.00 SiO_2 and 35.00 BaO:65.00 SiO_2.
[k] Prepared by mixing the appropriate amounts of the compositions 37.00 BaO:63.00 SiO_2 and 38.00 BaO:62.00 SiO_2.
[l] Prepared by mixing the appropriate amounts of the compositions 38.00 BaO:62.00 SiO_2 and 39.00 BaO:61.00 SiO_2.
[m] Prepared by mixing the appropriate amounts of the compositions 39.00 BaO:61.00 SiO_2 and $2BaO \cdot 3SiO_2$.

The present diagram (fig. 1b) differs from Eskola's in several important respects. It shows no solid solution. Instead, 2 discrete compounds occur: $5BaO \cdot 8SiO_2$, melting congruently at 1,446° C; and $3BaO \cdot 5SiO_2$, melting incongruently at approximately 1,423° C to form liquid and $5BaO \cdot 8SiO_2$. In addition, 2 eutectics are located at approximately 34-mole-percent BaO and 1,410° C and about 39-mole percent BaO and 1,437° C.

The exact location of the first eutectic relative to the 34-mole-percent BaO composition could not be established because nonequilibrium conditions prevailed for this composition. Specimens quenched from a comparatively large temperature range of about 10° contained 2 crystalline phases and glass. However, the 34- and 35-mole-percent BaO compositions definitely began melting at about 1,410° C, 10° below the melting point of $BaO \cdot 2SiO_2$, proving the existence of a eutectic in this region.

All compositions between 33.33-mole-percent BaO and 37.5-mole-percent BaO, when heated below the solidus, contained barium disilicate plus a second phase. The *d* values of barium disilicate remained essentially constant, indicating the absence of solid solution. A single phase was found to occur at the composition containing 37.5-mole-percent BaO, corresponding to the compound $3BaO \cdot 5SiO_2$. The X-ray diffraction powder pattern for this compound is given in table 4.

That the compound $3BaO \cdot 5SiO_2$ melts incongruently was ascertained by the observation that this phase does not occur in specimens heated above about 1,423° C. Above this temperature, for the composition range 37- to 38-mole-percent BaO, a new phase was detected in equilibrium with glass.

Below the solidus, for the composition 38-mole-percent BaO, the new phase occurs with $3BaO \cdot 5SiO_2$, whereas the specimen containing 39-mole-percent

TABLE 2. *X-ray diffraction data for the high temperature form of* $BaO{\cdot}2SiO_2$ (CuK_{α_1} *radiation*)

Levin and Ugrinic		Roth and Levin	
d[a]	I	d	I/I_o[b]
A	%	*A*	%
7.00	14	6.763	39
6.87	13		
5.63	17	5.514	21
4.75	12	4.696	23
4.15	8	4.118	17
4.02	77	3.981	93
3.57	52	3.539	74
3.39	14	3.331B	26
3.36	23		
3.27	25	3.250	31
		3.160	46
3.15	100	3.129	100
3.11	87	3.095	71
2.86	27	2.843	21
2.76	40	2.749	49
2.69	7	2.667	7
2.61	12	2.593	11
2.36	16	2.349	7
2.35	16	2.329	14
2.26	32	2.245	33
2.23	29	2.220	17
2.21	51	2.204	37
		2.198	46
2.16	25	2.155	31
2.06	21	2.059	19
2.05	32	2.040	29
2.00	7	1.992	7
1.923	12	1.916	34
		1.911	31
		1.876	9
1.877	17	1.870	11
		1.862	11
1.827	8	1.824	14
1.783	16	1.778	21
1.732	9	1.727	7
1.706	31	1.703	21
		1.669	7
		1.640	7
1.601	13	1.597	11
1.584	9	1.582	9
1.571	15	1.570	11
		1.560	13
		1.502	7
1.481	8	1.477	7
1.458	11	1.456	11
1.408	6	1.405	4
1.392	6	1.387	6
1.378	9	1.375	6
		1.362	10
		1.328	6
		1.306	6
1.292	16	1.290	9
1.288	16	1.286	13
1.285	10		
1.281	10	1.278	9

[a] The d values for this pattern are consistently larger than those found in the present work. As the two patterns were made from the same specimen, it seems likely that the X-ray diffraction equipment used for the older work was out of alinement.

[b] The intensities listed are given relative to the strongest peak.

TABLE 3. *X-ray diffraction powder pattern for the compound* $2BaO{\cdot}3SiO_2$

Indexed up to $d \sim 2.1$ ($CuK_{\alpha 1}$ radiation)

d	I/I_0[a]	$\frac{1}{d^2}$obs.	$\frac{1}{d^2}$cal.[b]	hkl
A	%			
12.44	4	0.0065	0.0064	100
6.948	20	.0207	.0207	001
6.204	5	.0257	.0256	200
			.0257	$10\bar{1}$
5.909	10	.0286	.0285	101
4.384	5	.0520	.0520	110
4.164	3	.0577	.0577	300
3.880	10	.0664	.0662	011
3.746	100	.0713	.0712	$21\bar{0}$
			.0713	$11\bar{1}$
3.669	60	.0743	.0743	$30\bar{1}$
3.469	5	.0831	.0827	002
3.409	7	.0861	.0865	$10\bar{2}$
3.299	50	.0919	.0919	102
3.249	55	.0947	.0946	211
3.123	30	.1026	.1026	400
3.125	30	.1030	.1029	$20\bar{2}$
			.1032	310
2.794	15	.1281	.1280	311
2.780	40	.1294	.1287	401
2.756	35	.1317	.1321	$11\bar{2}$
			.1323	$30\bar{2}$
2.597	10	.1482	.1481	410
2.495	5	.1606	.1603	500
2.475	5	.1633	.1634	$41\bar{1}$
2.391	5	.1749	.1744	$40\bar{2}$
2.343	20	.1821	.1822	020
2.305	5	.1883	.1885	$10\bar{3}$
			.1886	120
2.267	45	.1945	.1941	312
2.221	20	.2027	.2028	021
2.199	15	.2067	.2058	510
			.2078	220
2.177	5	.2110	.2106	121
2.132	90	.2200	.2199	203
			.2200	412
2.080	15			
2.076	17	[c]	[c]	[c]
2.033	8			
1.975	12			
1.970	17			
1.911	13			
1.874	11			
1.820	8			
1.806	6			
1.794	8			
1.780	14			
1.776	15			
1.753	7			
1.738	9			
1.703	3			
1.686	3			
1.648	8			
1.632	8			
1.628	8			
1.609	3			
1.598	3			
1.550	12			
1.508	7			

[a] I/I_0 represents the relative intensity of the diffraction peak relative to the strongest peak.

[b] These values were calculated on the basis of a unit cell size of $a = 12.51$ A, $b = 4.69$ A, $c = 6.97$ A, $\beta = 93°23'$.

[c] No attempt was made to index the rest of the pattern due to the large cell size and low symmetry of the material.

BaO contains the new phase and $2BaO{\cdot}3SiO_2$. Therefore the composition of the new compound occurs between 38- and 39-mole-percent BaO, most probably $5BaO{\cdot}8SiO_2$ (containing 38.46-mole-percent BaO). No change in the X-ray diffraction powder pattern (table 5) was observed up to the liquidus of $5BaO{\cdot}8SiO_2$ (1,446° C). The congruent melting point of the 5 : 8 compound is supported by the unequivocal existence of the eutectic at about 39-mole-percent BaO (see compositions containing 39- and 39.5-mole-percent BaO in table 1).

Figure 3 shows a schematic comparison of the X-ray diffraction powder patterns of $2BaO{\cdot}3SiO_2$, $5BaO{\cdot}8SiO_2$, and $3BaO{\cdot}5SiO_2$. One notable feature should be mentioned. With decreasing BaO content, from $2BaO{\cdot}3SiO_2$ to $3BaO{\cdot}5SiO_2$, the doublet in

TABLE 4.—*X-ray diffraction powder data for the compound* $3BaO{\cdot}5SiO_2$

($CuK\alpha_1$ radiation)

d	I/I_0[a]	*d*	I/I_0[a]
Å	%	Å	%
6.79	23	2.039	6
6.09	15	2.024	9
5.17	6	1.999	23
4.253	13	1.908	20
3.983	6	1.888	5
3.847	100	1.876	6
3.778	81	1.842	21
3.723	19	1.817	35
3.424	10	1.800	14
3.329	13	1.786	13
3.250	81	1.764	11
3.197	53	1.729	10
3.100	23	1.702	5
2.910	6	1.627	10
2.875	15	1.617	9
2.788	56	1.612	9
2.769	28	1.556	9
2.428	5	1.551	10
2.366	9	1.527	6
2.354	28	1.474	5
2.268	34	1.459	5
2.230	19	1.440	9
2.211	38	1.414	6
2.173	9	1.394	6
2.156	10	1.367	5
2.120	6	1.340	11
2.068	15		

[a] The intensity of these peaks is given relative to the height of the strongest peak.

$2BaO{\cdot}3SiO_2$, occurring at about $2\theta = 23.5°$ and 24° is shifted to a lower angle while the doublet at $2\theta = 27°$ and 28.5° is shifted to a higher value. This shift is discontinuous. Instead of a continuous shift in *d* values, as expected for solid solution, 2 phases of unvarying *d* values were always found for intermediate compositions. Therefore, it must be concluded that there is no appreciable solid solution in the $BaO{\cdot}2SiO_2$-$2BaO{\cdot}3SiO_2$ system.

4.4. Criticism of the Solid Solution Diagram

The reason for the differences between the present diagram and the continuous solid solution interpretation may be found in reviewing the method used and data obtained by Eskola [1].

TABLE 5. *X-ray diffraction powder data for the compound* $5BaO{\cdot}8SiO_2$.

($CuK\alpha_1$ radiation)

d	I/I_0[a]	*d*	I/I_0[a]
A	%	A	%
6.85	11	2.195	18
5.99	13	2.173	31
4.287	31	2.141	13
3.795	78	2.071	18
3.735	89	1.984	22
3.264	100	1.906	18
3.209	56	1.870	7
3.099	38	1.823	18
2.852	11	1.796	31
2.820	22	1.755	13
2.778	78	1.732	11
2.761	40	1.635	18
2.345	18	1.623	9
2.265	27	1.614	16
2.224	27	1.551	13

[a] I/I_0 represents the intensity of the diffraction peaks relative to the strongest peak.

Table 6 compares the melting point data reported by Eskola with those found in the present investigation. It may be seen that the liquidus values given by Eskola for the 3 intermediate compositions are 3.5° to 4.5° higher than the interpolated values obtained from figure 1(b), for the corresponding compositions. If only these compositions had been studied in the present investigation, essential agreement would have been obtained for the liquidus curve. However, an investigation of additional compositions revealed the existence of 2 eutectics, thus eliminating the possibility of complete solid solution. As solidus values obtained by the quenching technique in glass-forming systems are less accurate than liquidus values, especially for compositions remote from the eutectic, a difference of as much as 20° (table 6) is quite possible.

In table 7 the indices of refraction of the discrete phases found in the present study are compared with the values given by Eskola for 6 compositions. As in the case of the melting point data, if only these compositions are considered, solid solution would be indicated. However, the indices of refraction obtained by Eskola are compatible with the indices found for the discrete phases, identified in the present

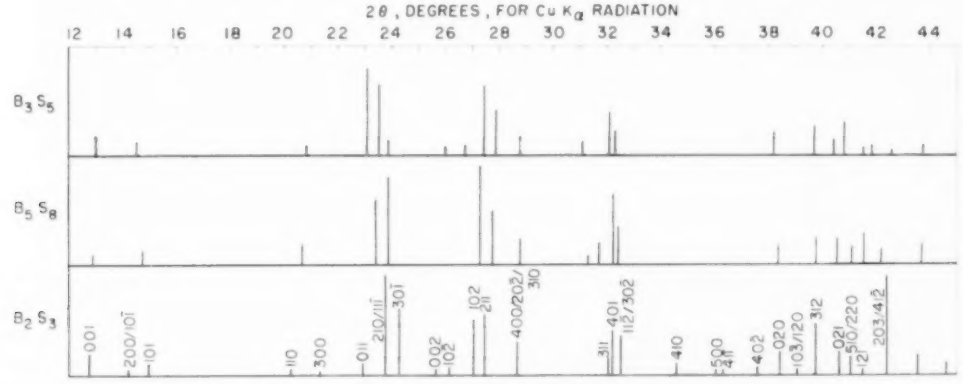

FIGURE 3. *Schematic X-ray diffraction powder patterns for the compounds* $3BaO{\cdot}5SiO_2$, $5BaO{\cdot}8SiO_2$, *and* $2BaO{\cdot}3SiO_2$.

work by X-ray methods. The interpretation of the indices for the specimen containing 35.11-mole-percent BaO, for example, is that the extreme indices reported by Eskola are the α for $BaO{\cdot}2SiO_2$ and the γ for $3BaO{\cdot}5SiO_2$.

In postulating solid solution, Eskola placed great reliance on the observation that for the mixture containing 37-mole-percent of BaO, crystals formed at temperatures below the solidus possessed lower indices than crystals formed above the solidus. However, the present diagram, in which the compound $3BaO{\cdot}5SiO_2$ is shown to melt incongruently to $5BaO{\cdot}8SiO_2$ and liquid, is equally consistent with this observation.

Concerning the polymorphism of $BaO{\cdot}2SiO_2$, the corresponding indices of refraction of the high and low forms are the same within the limits of accuracy of the immersion method (± 0.003). Thus the 2 forms are optically indistinguishable.

The conclusion that little or no solid solution exists in the binary system $BaO\text{-}SiO_2$, is in agreement with the opinions of Douglass [7], based on the structure of sanbornite. However, considerable solid solution has been postulated in $BaO{\cdot}2SiO_2$ with Al_2O_3 by Thomas [4] and with B_2O_3 by Levin and Ugrinic [5]. Such systems might be reviewed with the idea of detecting the presence of the 3:5 and 5:8 compounds within the ternary system. It seems likely that a further study of these, or other ternary systems involving BaO and SiO_2, would reveal that little solid solution occurs between any of the 4 compounds discussed here, involving a change in the ratio of the large cation to the tetrahedrally coordinated cation.

TABLE 6. *Comparison of melting point data for compositions in the system* $BaO{\cdot}2SiO_2$-$2BaO{\cdot}3SiO_2$

Composition		Liquidus		Solidus	
BaO	SiO_2	Eskola [1]	Roth & Levin [a]	Eskola [1]	Roth & Levin [a]
mole %	*mole %*	° *C*	° *C*	° *C*	° *C*
33.33	66.67	1,420	1,420		
35.11	64.89	[b] 1,433.5	1,429	[b] 1,421	1,410
37.02	62.98	[b] 1,445.5	1,442	[b] 1,433	1,410
38.25	61.75	[b] 1,449.5	1,445	[b] 1,439	1,423
40.00	60.00	[b] 1,449.5	1,447		

[a] Obtained from figure 1(b), to correspond to the listed compositions, which were studied by Eskola.
[b] Interpolated from data in table 2 of reference [1].

5. Summary

The phase equilibrium diagram for the subsystem $BaO{\cdot}2SiO_2$-$2BaO{\cdot}3SiO_2$ within the binary system $BaO\text{-}SiO_2$ has been revised. Fourteen compositions were studied by the quenching method. Phases were identified by X-ray diffraction powder patterns and with the aid of the polarizing microscope. The subsystem includes 4 binary compounds: the end-members, $BaO{\cdot}2SiO_2$ and $2BaO{\cdot}3SiO_2$, and 2 new compounds, $3BaO{\cdot}5SiO_2$ and $5BaO{\cdot}8SiO_2$. No perceptible solid solution was found between any of these compounds, contrary to previously published diagrams, which show complete solid solution between barium disilicate and dibarium trisilicate. Barium disilicate was found to have a quenchable and slowly reversible phase transformation at about 1,350° C. The mineral sanbornite corresponds to the low temperature form. The compound $5BaO{\cdot}8SiO_2$ and the end-member $2BaO{\cdot}3SiO_2$ melt congruently at 1,446° and 1,447° C, respectively. A eutectic exists between the 2 at about 1,437° C, and 39-mole-percent BaO. The compound $3BaO{\cdot}5SiO_2$ melts incongruently at about 1,423° C to form $5BaO{\cdot}8SiO_2$ and liquid. A eutectic between $BaO{\cdot}2SiO_2$ and $3BaO{\cdot}5SiO_2$ occurs at about 1,410° C and 34-mole-percent BaO. Dibarium trisilicate was found to be monoclinic with $a=12.51$ A, $b=4.69$ A, $c=6.97$ A, and $\beta=93°23'$.

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TABLE 7. *Comparison of optical data for compositions in the system* $BaO{\cdot}2SiO_2$-$2BaO{\cdot}3SiO_2$

(Indices of refraction by Eskola for continuous solid solution series; indices by Roth and Levin for discrete compounds)

Composition		Compound	Indices of refraction (λ_D, 30° C)						Sign and 2V	Index of quenched glass (30°)
BaO	SiO_2		Eskola [1]			Roth and Levin				
Mole %	*Mole %*									
33.33	66.67	L-$BaO{\cdot}2SiO_2$				1.596	1.612	1.621	Negative, large	
		H-$BaO{\cdot}2SiO_2$	1.597	1.612	1.621	1.596	1.611	1.619	Negative, 70°	1.608
35.11	64.89		1.597	1.612	1.636					
37.02	62.98		1.612	1.615	1.638					
37.50	62.50	$3BaO{\cdot}5SiO_2$				1.612	1.616	1.636	Positive, 35°	1.625
38.25	61.75		1.616	1.620	1.639					
38.46	61.54	$5BaO{\cdot}8SiO_2$				1.617	1.622	1.638	Positive, 40°	1.629
39.50	60.50		1.619	1.624	1.644					
40.00	60.00	$2BaO{\cdot}3SiO_2$	1.620	1.625	1.645	1.618	1.623	1.643	Positive, 35°	1.635

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Separation and Determination of Phosphate, Silicate, and Arsenate

W. Stanley Clabaugh and Audrey Jackson

A method was developed for quantitatively separating and determining phosphate, silicate, and arsenate when they occur together in solution. All three, at a *p*H of 1.8, form heteropoly molybdate complexes when heated just to boiling. Only the phosphate complex is extracted into ether from a solution that contains one volume of concentrated hydrochloric acid plus nine volumes of solution. After removing the phosphate, only the silicate complex is extracted into butanol from a solution that contains two volumes of concentrated hydrochloric acid plus nine volumes of solution. The arsenate complex is then extracted into methyl isobutyl ketone after readjusting the acidity back to 1+9 by adding silica-free ammonium hydroxide. The various complexes are reduced by adding stannous chloride to the organic solvent and determined spectrophotometrically. The effect of various salts on the complex formation and the extraction is also reported

1. Introduction

The heteropoly-complex compounds of molybdenum have been known and used by chemists for more than a century.[1] They are used by analytical chemists especially for determining phosphorus, silicate, and arsenate, either as the yellow complexes or as the reduced blue complexes.

The molybdenum salt most frequently used to form these complexes is the so-called ammonium molybdate. For this reagent to be most useful it must not contain, either individually or combined, excessive amounts of phosphate, silicate, and arsenate. The Committee on Analytical Reagents of the American Chemical Society has published a specification for ammonium molybdate.[2] This specification has, in addition to other requirements, a requirement and test for phosphate but not for silicate or arsenate. While trying to improve the test for phosphate and also limit the amount of silicate and arsenate that might be present, it was found that all three of the ions in question could be collectively determined. It was also found that they could be quantitatively separated from one another even though they were contained in the same solution.

The extensive literature concerned with the determination of these ions, which contains so many articles that it is impractical to enumerate them all, is largely the result of the effort to ascertain and control the many variables which influence the formation and reduction of a specific, desired complex. For a partial résumé of the difficulties, see the preprint of an article by Mellon.[3]

Analysts have also used various organic solvents, or mixtures of organic solvents, to extract the desired complex.[4] To the authors' knowledge, a satisfactory method has not been published for separating and determining all three ions, phosphate, silicate, and arsenate, when they occur together in a solution. Such a method has now been developed and the details are given below.

2. Reagents and Standards

2.1. Ammonium Hydroxide (Silica-Free)

The ammonium hydroxide used must be free from silica. Aqueous ammonia in contact with glass, even momentarily, will dissolve a sufficient amount of silica to make it unusable for the purpose here described. Since all ammonium hydroxide available commercially comes in glass containers, one must prepare silica-free ammonium hydroxide in the laboratory. The most convenient method to do this is to saturate distilled water with ammonia gas from a cylinder of compressed anhydrous ammonia. Plastic tubing and bottles must be used throughout.

2.2. Ammonium Molybdate Solution (10 Percent)

Prepare a solution of ammonium molybdate by dissolving 10 g of the ACS reagent in 100 ml of distilled water. This solution should be prepared daily and placed in polyethylene containers.

To determine the suitability of each lot of ammonium molybdate, dissolve 2.5 g of the reagent in 80 ml of distilled water, add a few drops of bromine water, and adjust the *p*H of the solution to 1.8 with diluted hydrochloric acid (1+9). Heat the solution just to boiling and cool it to room temperature. Add 10 ml of concentrated hydrochloric acid and 1 ml of butanol. Extract the combined phosphate, silicate, and arsenate complexes with methyl isobutyl ketone. After washing the ketone

[1] L. Svanberg and H. Strume, J. prakt. Chem. **44**, 257 (1848).
[2] Reagent Chemicals, American Chemical Society, Specifications 1955.
[3] M. G. Mellon, Analytical properties of heteropoly anions, presented at a Symposium on Structure and Properties of Heteropoly Anions, Division of Physical and Inorganic Chemistry, American Chemical Society (September 1956).
[4] N.A. Fillipova and L.I. Kuznetsova, Zavodskaya Lab., **16**, 536 (1950); C. Wadelin and M. G. Mellon, Analyst **77**, 708 (1952); C. H. Lueck and D. F. Boltz, Anal. Chem. **30**, 183 (1958).

solution and reducing the molybdenum complexes as described later (3.4), any blue color in the ketone should not exceed that produced when 0.01 mg of silica and 0.5 g of the same ammonium molybdate are treated exactly as was the 2.5 g of the ammonium molybdate.

2.3. Stannous Chloride Solution

Prepare a solution of stannous chloride by dissolving 2 g of the ACS reagent $SnCl_2 \cdot 2H_2O$ in concentrated hydrochloric acid and diluting it to 100 ml with concentrated hydrochloric acid.

2.4. Phosphate Solution (0.01 mg of PO_4 in 1 ml)

Prepare a stock solution by dissolving 0.143 g of assayed potassium dihydrogen phosphate, KH_2PO_4, in distilled water and diluting the resulting solution to 100 ml. Dilute 10 ml of this stock solution to 1,000 ml. Since the *p*H of this solution is approximately 4, it is safe to prepare and store it in glass vessels.

2.5. Silicate Solution (0.01 mg of SiO_2 in 1 ml)

Prepare a stock solution of silica by dissolving 9.46 g of assayed $Na_2SiO_3 \cdot 9H_2O$ in 9 ml of silica-free ammonium hydroxide and diluting the resulting solution to 200 ml (199.4 g at 25° C) with distilled water. Dilute a 1-ml aliquot of this solution plus 5 ml of silica-free ammonium hydroxide to 1,000 ml (997.1 g at 25° C) with distilled water. Since volumetric polyethylene ware was not available, the silica solution was diluted on the weight basis.

2.6. Arsenate Solution (0.01 mg of As in 1 ml)

Prepare a stock solution of arsenic by dissolving 0.132 g of NBS standard sample of As_2O_3 in 10 ml of diluted hydrochloric acid (1+1) to which bromine water is added. To prevent loss of arsenic by volatilization, sufficient bromine must be present at all times to impart a strong yellow color to the solution. This may require the addition of more bromine water while the arsenic trioxide is dissolving. Dilute the resulting solution to 1,000 ml. Dilute 100 ml of this stock solution, to which 5 ml of concentrated hydrochloric acid has been added, to 1,000 ml. Since these solutions are acid, they can be prepared, diluted, and stored in glass vessels.

3. General Procedure

3.1. Formation of the Heteropoly Complexes

Dissolve the sample to be analyzed in 80 ml of distilled water and add 5 ml of a 10-percent solution of ammonium molybdate. Adjust the acidity of the solution to approximately *p*H 4 by adding silica-free ammonium hydroxide or hydrochloric acid as required.

If the solution of the unknown is alkaline, it must be prepared in a platinum container to prevent contamination from dissolved silica. After the solution has been adjusted to *p*H 5 or less, as determined with indicator paper, it may be transferred to a glass vessel without danger of dissolving sufficient silica to interfere with the test.

Add enough bromine water to impart a slight yellow color to the solution. The bromine water is added to oxidize the arsenic to the quinquevalent state, because tervalent arsenic does not form a heteropoly complex with molybdate. Readjust the acidity of the solution to *p*H 1.7 to 1.9. Heat the resulting solution just to boiling, cool it to room temperature, and dilute it to 90 ml. Make all *p*H measurements which are less than 7 with a standardized glass electrode system. Do not use glass electrodes in alkaline solutions because sufficient silica may be dissolved to vitiate the results of the test for silica.

3.2. Separation and Determination of Phosphate

Transfer the solution which was prepared as described above to a separatory funnel and add 10 ml of concentrated hydrochloric acid and 35 ml of ethyl ether. Shake the mixture vigorously for a few minutes and allow the two layers to separate. Draw off the aqueous layer and reserve it for the determination of silica and arsenic. Wash the ether layer twice with 10-ml portions of diluted hydrochloric acid (1+9). Draw off and discard the aqueous layers. Add 0.2 ml of the stannous chloride solution to the ether solution and shake the mixture. Dilute the ether solution to 25 ml with more ether and determine its optical density with a spectrophotometer at 630 mμ. Determine the amount of phosphate present from a calibration curve. If greater sensitivity is desired, measurements may be made at approximately 830 mμ.

3.3. Separation and Determination of Silica

Add 10 ml of concentrated hydrochloric acid to the aqueous solution reserved from the separation of phosphate and transfer it to a separatory funnel. Pour into the solution 50 ml of butanol, shake the mixture vigorously, and allow the layers to separate. Draw off the aqueous layer and add to it 10 ml of silica-free ammonium hydroxide and reserve this solution for the extraction and determination of arsenic.

Wash the butanol layer three times with 20-ml portions of diluted hydrochloric acid (1+99). Draw off and discard the aqueous layers. Add 0.5 ml of the stannous chloride solution to the butanol solution and shake the mixture. Dilute the butanol solution to 50 ml with more butanol and determine its optical density with a spectrophotometer at 630 mμ. Determine the amount of silica present from a calibration curve.

The optical density should be determined immediately after the reduction by stannous chloride. If this is not done, the blue color begins to fade, but treatment with stannous chloride as described above will restore the blue color to its original intensity.

This fading may be attributed to some impurity in the butanol, because the reduced molybdenum blue color was found to be stable for 24 hr or more in some lots of butanol.

3.4. Separation and Determination of Arsenic

Transfer to a separatory funnel the aqueous solution reserved from the separation of silica, to which 10 ml of silica-free ammonium hydroxide had been added. Pour into the solution 25 ml of methyl isobutyl ketone, shake the mixture thoroughly, and allow the layers to separate. Draw off and discard the aqueous layer. Wash the ketone solution three times with 10-ml portions of diluted hydrochloric acid (1+9). Draw off and discard the aqueous layers. Add a freshly prepared solution of 0.2 ml of the stannous chloride solution in 10 ml of water to the ketone solution, shake the mixture, and allow the layers to separate. Draw off and discard the aqueous layer. If the ketone layer is cloudy, it may be cleared by washing it with diluted hydrochloric acid (1+99). Dilute the ketone solution to 30 ml with more ketone and determine its optical density with a spectrophotometer at 630 mμ. Determine the amount of arsenic present from a calibration curve.

3.5. Reliability of the Method

The calibration curves shown in figures 1, 2, and 3 were determined for each of the complexes studied. The optical densities were determined at a wavelength of 630 mμ with a spectrophotometer provided with absorption cells that were 50 mm long. The partition coefficients for the various complexes were not determined. However, when quantities of the three ions were present in considerable excess of 30 mg each, each one was completely extracted in a single operation as specified. To obtain complete extraction of the arsenic in one operation with methyl isobutyl ketone, the aqueous phase must be saturated with butanol.

The reliability of the method was ascertained by preparing synthetic solutions containing known amounts of the three elements and subsequently separating them and determining the amount of each. The results of the experiments are given in table 1.

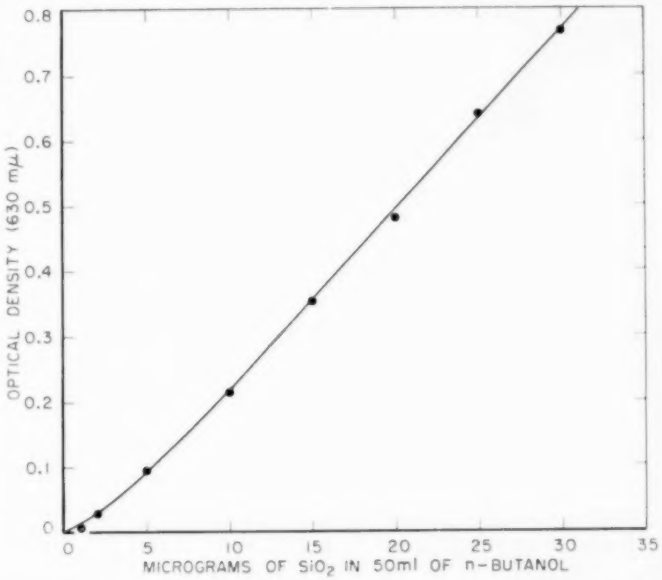

FIGURE 2. *Calibration curve for reduced molybdosilicate in butanol.*

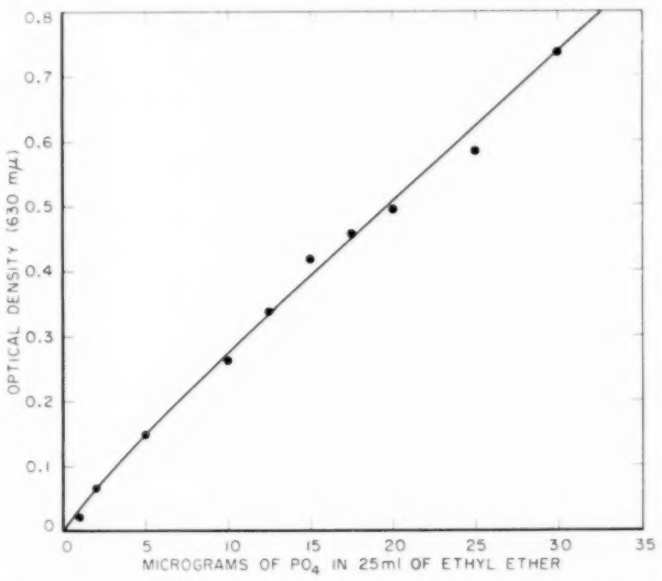

FIGURE 1. *Calibration curve for reduced molybdophosphate in ethyl ether.*

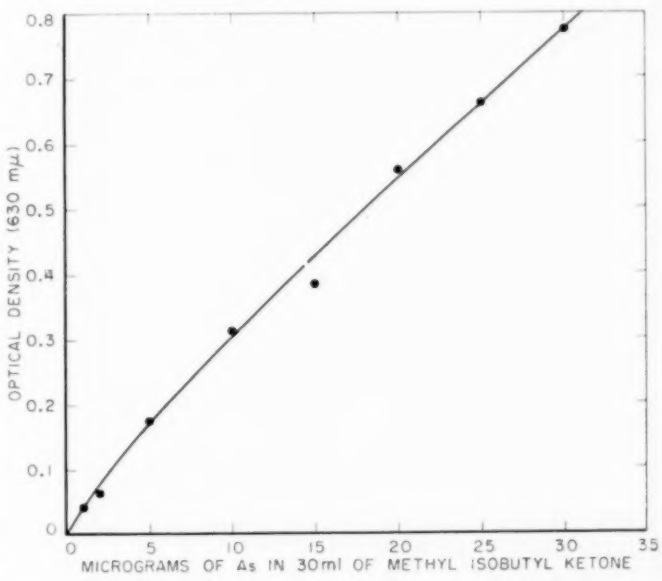

FIGURE 3. *Calibration curve for reduced molybdoarsenate in methyl isobutyl ketone.*

TABLE 1. *Separation and determination of known quantities of phosphate, silicate, and arsenate*

Solution No.	Phosphate (PO_4)		Silicate (SiO_2)		Arsenate (As)	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	μg	μg	μg	μg	μg
1	1	1	1	1	1	1
2	10	10	10	10	10	10
3	30	30	30	30	30	30
4	30	30	2	2	2	2
5	2	2	30	30	2	2
6	2	2	2	2	30	29

4. Interference of Salts in the Extractions

To determine the effect of salt concentration on the accuracy of the determinations, experiments were made by adding 10 mg of each of the three elements to solutions of various salts. The amounts of salts taken were 1, 2, and 5 g, which would correspond to 1, 2, and 5 percent at the start of the extraction of phosphate by ethyl ether.

4.1. Extraction From Solutions Containing 1 g of salt

Complete recovery was obtained when 10 μg of each of the three ions in question was added to 1 g of each of the following salts: Ammonium carbonate, chloride, nitrate, and sulfate; sodium carbonate, chloride, hydroxide, nitrate, perchlorate, and sulfate; potassium carbonate, chloride, hydroxide, nitrate, and sulfate; and ferric chloride. When sodium or potassium acetate was used, the acetate ion interfered with the recovery of phosphate. If the acetate was converted to nitrate by evaporating to dryness several times in the presence of nitric acid, the added phosphate was recovered. Recoveries of silicate and arsenate and the effect that salts of other organic acids might have on the reaction were not investigated.

4.2. Extraction From Solutions Containing 2 g of Salt

When the quantities of the above salts, except ferric chloride which was not tried, were increased to 2 g, complete recoveries of the added phosphate, silicate, and arsenate were obtained unless the anion was chloride. In addition, 2 g of calcium chloride and barium nitrate were tried and the calcium and barium did not interfere. Complete recovery of the three ions was obtained from 2 g of the chloride salts if the initial acidity of the solution was adjusted to a *p*H of 1.7 to 1.9 with diluted sulfuric acid instead of with diluted hydrochloric acid. The other conditions remained as described.

4.3. Extraction From Solutions Containing 5 g of Salt

a. Extraction From Nitrate Solutions

Experiments were made to determine the recoverability of phosphate, silica, and arsenic from solutions containing 5 g each of ammonium nitrate, sodium nitrate, potassium nitrate, barium nitrate, calcium nitrate, and aluminum nitrate. The results are given in table 2.

b. Extraction From Sulfate Solutions

Experiments were made to determine the recoverability of phosphate, silica, and arsenic from solutions containing 5 g each of ammonium sulfate, sodium sulfate, potassium sulfate, and aluminum sulfate. The results are given in table 3.

TABLE 2. *Separation and determination of phosphate, silicate, and arsenate from solutions containing 5 g of nitrate salts*

Salt	Phosphate		Silicate		Arsenate	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	μg	μg	μg	μg	μg
NH_4NO_3	10	10	10	11	10	9
$NaNO_3$	10	11	10	10	10	10
KNO_3	10	9	10	11	10	12
$Ba(NO_3)_2$	10	12	10	9	10	9
$Ca(NO_3)_2$	10	9	10	11	10	9
$Al(NO_3)_3 \cdot 9H_2O$	10	12	10	10	10	10

TABLE 3. *Separation and determination of phosphate, silicate, and arsenate from solutions containing 5 g of various sulfates*

Salt	Phosphate		Silicate		Arsenate	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	μg	μg	μg	μg	μg
$(NH_4)_2SO_4$	10	5	10	10	10	10
Na_2SO_4	10	4	10	12	10	10
K_2SO_4	10	3	10	12	10	11
$Al_2(SO_4)_3 \cdot 18H_2O$	10	4	10	10	10	9

It is seen that whereas the recovery of silica and of arsenic was satisfactory, only one-third to one-half of the added phosphate was recovered. It was found, however, that by operating in a less acid solution than that originally specified, extraction and recovery of phosphate could be accomplished from the solutions containing 5 g of sulfates. Depending on the particular sulfate, from 80 to 86 percent of the original volume of hydrochloric acid sufficed.

To remove the silica complex, the acidity of the solution was increased to a concentration of (2+9), which was the concentration originally specified for the extraction of silica. To extract arsenic, the acidity was then reduced by the addition of silica-free ammonium hydroxide to that found experimentally suitable for the extraction of phosphate. The results, given in table 4, show that phosphate, silica, and arsenic can be separated from one another and completely recovered in the presence of 5 g of various sulfate salts.

TABLE 4. *Recovery of 10 μg each of phosphate, silicate, and arsenate added to solutions containing 5 g of various sulfates by the modified method*

Salt	Phosphate		Silicate		Arsenate	
	Concentrated HCl	PO_4 recovered	Concentrated HCl	SiO_2 recovered	Concentrated NH_4OH	As recovered
	ml	*μg*	*ml*	*μg*	*ml*	*μg*
$(NH_4)_2SO_4$	8.0	11	12.0	11	12.0	9
Na_2SO_4	8.6	10	11.4	11	11.4	8
K_2SO_4	8.0	10	12.0	11	12.0	11
$Al_2(SO_4)_3 \cdot 18H_2O$	8.5	11	11.5	11	11.5	9

c. Extraction From Chloride Solutions

Experiments were made to determine the recoverability of phosphate, silica, and arsenic from solutions containing 5 g each of ammonium chloride, sodium chloride, potassium chloride, barium chloride, calcium chloride, and aluminum chloride. The operating conditions were those specified in section 3. The results are given in table 5.

TABLE 5. *Separation and determination of phosphate, silicate, and arsenate added to solutions containing 5 g of various chlorides*

Salt	Phosphate		Silicate		Arsenate	
	Added	Recovered	Added	Recovered	Added	Recovered
	μg	*μg*	*μg*	*μg*	*μg*	*μg*
NH_4Cl	10	2	10	12	10	9
NaCl	10	3	10	11	10	11
KCl	10	4	10	9	10	12
$BaCl_2 \cdot 2H_2O$	10	7	10	11	10	11
$CaCl_2 \cdot 2H_2O$	10	7	10	10	10	11
$AlCl_3 \cdot 6H_2O$	10	1	10	10	10	10

The results show that the phosphate was not completely recovered. However, the amount of phosphate remaining in solution did not seriously interfere in the determination of either silica or arsenic.

Attempts were then made to modify the original procedure in the manner similar to that followed for solutions containing 5 g of sulfate salts. That is, the acidity at which the phosphate could be quantitatively extracted was established experimentally. This acidity was found to be lower than that for the sulfate salts. To extract the silica the acidity was increased to (2+9), the original concentration specified for the extraction of molybdosilicate. Finally, to extract the arsenic the acidity was again lowered to that required to extract the molybdophosphate, as determined experimentally for a particular chloride salt. Complete recovery of phosphate and of silica was obtained, but not of arsenic. These results are given in table 6.

Even when an amount of nitric acid, 7.5 ml, was substituted for the 10 ml of hydrochloric acid, the recovery of arsenic remained incomplete.

TABLE 6. *Separation and determination of 10 μg each of phosphate, silicate, and arsenate added to solutions containing 5 g of various chlorides by the modified method*

Salt	Phosphate		Silicate		Arsenate	
	Concentrated HCl added	PO_4 recovered	Concentrated HCl added	SiO_2 recovered	Concentrated NH_4OH added	As recovered
	ml	*μg*	*ml*	*μg*	*ml*	*μg*
NH_4Cl	4.0	11	16.0	11	10.0	6
NaCl	7.0	12	13.0	11	10.0	5
KCl	5.5	11	14.5	10	10.0	6
$BaCl_2 \cdot 2H_2O$	8.0	12	12.0	11	10.0	9
$CaCl_2 \cdot 2H_2O$	8.5	11	11.5	9	10.0	7
$AlCl_3 \cdot 6H_2O$	7.0	12	13.0	10	10.0	5

The determination of all three elements in question when 5 g of a chloride salt is present requires two procedures. One procedure, that by which the results reported in table 5 were obtained, is to determine the silica and arsenic. The other procedure, that by which the results reported in table 6 were obtained, is to determine the phosphate and silica. It should be noted that silica may be determined by either method.

It should be emphasized that the separation and determination of the silica appeared to be complete regardless of the salt concentration, provided the molybdosilicate complex was extracted with butanol from a solution that contained 2 volumes of concentrated hydrochloric acid plus 9 volumes of solution.

5. Discussion of Results

The procedure described in section 3 is suitable for the quantitative separation of small amounts of phosphate, silica, and arsenic from one another and for their subsequent determination when they occur in solutions containing as much as 1 g in 100 ml of solution of either a chloride, nitrate, sulfate, or perchlorate.

If the quantity of salt is increased to 2 g, complete separation and recovery is effected except in the case of a chloride salt.

In the presence of 5 g of either a sulfate or chloride salt, the extraction of phosphate is incomplete. By lowering the acidity at which the phosphate is extracted, then establishing the acidity originally specified for the extraction of silica, and finally, to extract the arsenic, reestablishing the acidity found suitable for the extraction of the phosphate, the three substances in question can be quantitatively separated from one another even in the presence of 5 g of a sulfate salt. By following a similar procedure in the case of 5 g of a chloride salt, phosphate and silica can be successfully extracted and determined, but not the arsenic. It becomes necessary, in the case of 5 g of a chloride salt, to determine phosphate and silica in one solution and silica and arsenic in another.

WASHINGTON, February 2, 1959.

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Heat of Formation of Potassium Calcium Silicate

Edwin S. Newman

The heats of solution of $2CaO{\cdot}SiO_2$ (c, β), $CaSO_4$ (c, anhydrite), K_2SO_4 (c, II) and six members of a series of substitutional solid solutions of K_2O in dicalcium silicate were determined in a nitric-hydrofluoric acid mixture by means of an isothermal-jacket calorimeter. From these data and heats of formation taken from the literature, the heat of formation of $K_2O{\cdot}23CaO{\cdot}12SiO_2$ (c) was calculated to be $-6{,}420$ kilocalories per mole at 25° C.

1. Introduction

As part of a continuing investigation of the thermochemical properties of substances occurring in hydraulic cements and their reaction products, the heat of formation of $K_2O{\cdot}23CaO{\cdot}12SiO_2$, abbreviated $KC_{23}S_{12}$,[1] has been determined. No prior thermochemical data for this compound have been found.

Measurements were made at 25° C of $-\Delta H$, the heat evolved in the reaction

$$K_2O{\cdot}23CaO{\cdot}12SiO_2\ (c)+CaSO_4\ (c,\ anhydrite)\longrightarrow 12(2CaO{\cdot}SiO_2)\ (c,\ \beta)+K_2SO_4(c,\ II). \quad (1)$$

This reaction occurs spontaneously at high temperature [1],[2] where, however, the high-temperature form of $CaSO_4$ is present and liquid K_2SO_4 is formed. The value of $-\Delta H$ was obtained by measuring the heats of solution of these four substances in a mixture of nitric and hydrofluoric acid solutions. The heat of formation of $KC_{23}S_{12}$ at 25° C was calculated from the heat of the reaction and the heats of formation of the other three substances taken from the literature.

2. Materials, Apparatus, and Procedure

Analytical reagents were used in all preparations. Dicalcium silicate, C_2S, was made by the repeated heating at 1,450° C and dusting[3] of a mixture of low-alkali $CaCO_3$ and silicic acid. This material was stablized in the beta form by the addition of about 0.5 percent of B_2O_3 as H_3BO_3 and further heating and grinding. The final product was ground rapidly to pass a No. 100 sieve and stored in a desiccator over magnesium perchlorate and Ascarite.

Potassium sulfate was ground to pass a No. 100 sieve and heated overnight at 220° C. Precipitated gypsum was heated overnight at 1,000° C to convert it to anhydrite. Both of these materials were also stored in the desiccator until tested.

The potassium-containing compound in portland cement clinker, identified by Taylor [2] as $KC_{23}S_{12}$, is now believed to be a solid solution [3] in which K_2O is partially substituted for the CaO in dicalcium silicate. To prepare a series of such solid solutions, six mixtures of $CaCO_3$, silicic acid, and a glass of the composition $K_2O{\cdot}4SiO_2$ were heated repeatedly at 1,450° C with intervening grinding. These mixtures were prepared with various amounts of K_2O, the molar ratio of $(CaO+K_2O)/SiO_2$ being maintained at 24/12 (table 1). When microscopical examination indicated that each of these preparations consisted of a single phase, they were rapidly ground to pass a No. 100 sieve and stored in the desiccator until their heats of solution had been determined. The samples were analyzed by the conventional methods for portland cement [4], except that in the determination of SiO_2 in the dicalcium silicate sample, boron was removed by repeated evaporation with methyl alcohol.

The calorimeter and details of its operations have been described previously [5, 6, 7], but a number of minor changes have been made. The heater now consists of a 90-ohm coil of No. 32 double-silk insulated alloy wire in a platinum tube about $\frac{5}{32}$ in. in diameter and 5 in. long. A 4-blade platinum propeller-type stirrer is used in a platinum stirring tube, and the reaction vessel and its cover have been lined with sheet platinum. The heater current, from a bank of storage batteries, is controlled by means of one blade of a 50-amp double-pole double-throw spring toggle switch. Current from a dry cell through the other blade of the switch actuates one pen of a 3-pen tape chronograph. A second pen inscribes a standard seconds signal on the tape which travels at about 1 cm/sec. The maximum timing error probably does not exceed 0.03 sec in 10 min, or 1 part in 20,000. When the switch is in the off position, the heater current is stabilized by discharge through an external resistor. The heater current and voltage, about 0.2 amp and 18 v, respectively, are measured by means of a high-precision potentiometer, a standard 1-ohm resistor, and a volt box. These resistors have been calibrated from time to time by the Electrical Division of the Bureau. Temperature rises are measured with a platinum resistance thermometer, a Mueller G–1 bridge, and a high-sensitivity galvanometer with an optical lever of about 8 m. The apparatus is located in a constant-

[1] The customary abbreviations C for CaO, K for K_2O, and S for SiO_2 will be used.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] In the absence of stabilizers, the beta form of C_2S inverts to the gamma form at room temperature. The 10-percent increase in volume accompanying this inversion results in the disintegration or "dusting" of the particles into a fine powder. When a stabilizer is added, this dusting does not occur, and grinding is necessary to obtain a powdered material.

TABLE 1. *Analyses of preparations*

	Sample							
	β-C_2S	A	B	C	D	E	F	G[a]
	%	%	%	%	%	%	%	%
SiO_2	34.42	34.54	34.56	34.62	34.34	34.72	34.84	33.99
R_2O_3	0.10	0.28	0.26	0.30	0.12	0.32	0.18	----
CaO	65.01	64.42	64.16	63.32	62.46	59.34	60.66	61.14
MgO	.02	----	----	----	----	----	----	----
K_2O	----	0.47	0.93	1.69	2.95	5.65	4.30	4.16
Na_2O	----	.05	.05	.06	.06	.09	.08	----
Total	99.55	99.76	99.96	99.99	99.93	100.12	100.06	99.29
K_2O lost	----	18	18	25	34	36	35	57
	Molar proportions							
CaO	24.27	23.97	23.86	23.51	23.38	21.96	22.38	23.12
K_2O	----	0.104	0.206	0.373	0.657	1.245	0.944	0.936
SiO_2	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
(K_2O+CaO)	----	24.07	24.07	23.88	24.04	23.20	23.32	23.05

[a] This sample prepared from K_2CO_3, $CaCO_3$, and silicic acid.

temperature room operated at 25.0±0.5° C during calorimetric measurements. Temperature readings are taken at 2-min intervals during the rating periods and at 1-min intervals during the rapid-rise portion of the experimental period, with integration of the time-temperature curve by application of the trapezoidal rule to the recorded values. The errors introduced in the corrected temperature rise by the departure of this calculated curve from the true indicated time-temperature curve (obtained occasionally by means of the chronograph) are in part compensating and are negligible in comparison with the total error.

In the heat-of-solution determinations, the materials were dissolved in 600.0 g of a mixture of 11 ml of 48-percent HF with 587 g of 2.000 *N* HNO_3. The weights of the calorimeter samples were calculated according to the stoichiometry of eq (1), based on a sample weight of C_2S of 0.7000 g. This quantity dissolved in 600.0 g of acid solution gave the same sample ratio as the 0.49 g of C_2S dissolved in 420 g of solution, found by Brunauer, Kantro, and Weise [8] to give clear solutions and regular values for the heat of solution. The calculated sample weights were 0.7129, 0.0461, and 0.0590 g for $KC_{23}S_{12}$, calcium sulfate, and potassium sulfate respectively.

In order to make certain that the final calorimeter solutions for the reactants and for the products of eq (1) were identical, both of the reactants were dissolved consecutively in the same solution, the silicate being dissolved first. The same procedure was followed for the products, using a fresh calorimeter charge. Because of the very small heat effects caused by the small samples of $CaSO_4$ and K_2SO_4, the calorimeter was heated to approximately the convergence temperature (25.17° C) before these samples were dissolved, in order to keep the rate of temperature change of the calorimeter as small as possible during the rating periods. The precision of these measurements with small samples was low, since 1-mm deflection on the galvanometer scale corresponded to about 0.04 cal, or about 20 percent of the smallest effect measured. It was thought that the predissolving of 0.7000 g of C_2S (or 0.7129 g of $KC_{23}S_{12}$), corresponding to about 0.008 mole of CaO and 0.004 mol of SiO_2, might have no detectable effect on the heats of solution of the sulfates, since the calorimeter charge consisted of 0.30 mole of HF, 1.10 mole of HNO_3, and 29.10 mole of H_2O. The use of larger samples would result in better precision, although some account might have to be taken of the change of heat of solution with change of sample size. The heats of solution of larger samples, of several sizes, of $CaSO_4$ and K_2SO_4 in the nitric-hydrofluoric acid mixture were therefore determined without previously dissolving the silicates.

The use of standard substances for the calibration of calorimeters is desirable, since thereby the time-temperature curves during calibration and during use are similar. Such a standard substance for the calibration of heat-of-solution calorimeters using the nitric-hydrofluoric acid mixture [4, 9] is heat-treated zinc oxide of analytical reagent quality. For this purpose the zinc oxide is heated at 950° C for 1 hr and ground to pass a No. 100 sieve. A weighed sample is reheated for 5 min before use and cooled in a desiccator. The heat of solution of this zinc oxide at 25° C is 256.6 cal/g [4, 9]. This value, however, was determined for a ratio of zinc oxide to acid mixture of 7/425, and the resulting temperature rise is about 4.5° C. As a useful means of future calibration of such calorimeters for smaller temperature rises, and as a check on the present work, the heat of solution of the standard zinc oxide was determined using samples of 1.56 and 0.20 g in 600.0 g of nitric-hydrofluoric acid mixture in the electrically calibrated calorimeter. The corresponding temperature rises were about 0.7 and 0.09° C, respectively.

3. Experimental Results

The compositions of the samples as determined by analysis are given in table 1. It will be seen that from 18 to 36 percent of the K_2O added was lost by volatilization during the preparation of the samples, the percentage loss increasing with increase of K_2O

content. Allowance for the expected loss was made when the samples were proportioned. Six of the completed preparations had ratios of $(CaO+K_2O)/SiO_2$ from 23.88/12 to 24.27/12. The heats of solution of these six samples were used in determining the calculated heats of solution of C_2S and $KC_{23}S_{12}$.

The results of the electrical calibrations and the heat-of-solution measurements are given in tables 2, 3, 4, and 5. The negative sign before values in these tables indicates that the heat of solution was endothermic. The heats of solution of the eight silicate preparations (table 5) are plotted in figure 1 as a function of the percentage of K_2O in the samples. The heats of solution of samples E and F, somewhat deficient in cations, with (C+K)/S ratios of 23.20/12 and 23.32/12, respectively, were less than expected from the values of the other samples. A second-power curve was drawn through the data of figure 1 by the method of least squares, omitting the data for E and F. The average experimental heats of solution of C_2S and sample G, which was close to $KC_{23}S_{12}$ in composition, were 564.8 ± 0.19 and 569.3 ± 0.50 cal/g, respectively (see table 5). The heats of solution of C_2S and $KC_{23}S_{12}$ calculated from the equation of the curve, 565.11 and 568.86 cal/g, respectively, were used to determine $-\Delta H$ of reaction 1. Brunauer, Hayes, and Hass [10] gave the heat of solution of C_2S as 564.0 ± 2. cal/g, and the value taken from figure 2, p. 774 of the paper by Brunauer, Kantro, and Weise [8] is about 565 cal/g. These values are essentially the same as that obtained for C_2S in the present work.

TABLE 2. *Calibration experiments*

Calorimeter charge, 11 m of 48 percent HF solution and 587 g of 2.000 N HNO_3. Total weight 600.0 g

Electrical calibrations		Heat of solution of zinc oxide at 25° C			
Temperature rise	Electrical energy equivalent	Sample weight	Heat of solution	Sample weight	Heat of solution
Ohms	*cal/Ohm* [a]	*g*	*cal/g*	*g*	*cal/g*
0.06957$_2$	5754.$_1$	1.5619	256.82	0.2014	256.8
.06937$_1$	5757.$_0$	1.5653	256.88	.2023	257.9
.06948$_0$	5759.$_0$	1.5647	257.02	.2021	256.3
.06929$_0$	5757.$_3$				
.06921$_4$	5761.$_4$				
.06937$_2$	5757.$_4$				
Average	[b] 5757.7		256.91		257.0
S.D. [c]	0.98		0.06		0.48
C_v [d]	.017		.023		.19

[a] 1 cal = 4.184 abs j.
[b] $dP/dT = 0.1010$. The energy equivalent is therefore 581.5 cal/deg.
[c] S.D. = standard deviation of the average = $\sqrt{[\Sigma r^2-(\Sigma r)^2/n]/n(n-1)}$.
[d] Coefficient of variation = 100×S.D./(average).

TABLE 3. *Heat of solution of* $CaSO_4$ *(anhydrite) in 600.0 g of nitric-hydrofluoric acid at 25° C.*

(11 ml of 48% HF and 587 g of 2.000 *N* HNO_3)

Sample weight	Heat of solution	Sample weight	Heat of solution [b]	Sample weight	Heat of solution [c]	Sample weight	Heat of solution [d]
g	*cal/g*	*g*	*cal/g*	*g*	*cal/g*	*g*	*cal/g*
2.0175	−4.31	0.5091	−4.21	0.1014	−4.69	0.0494	−4.2$_3$
		.5230	−4.34	.1059	−5.22	.0498	−2.9$_9$
1.0450	[a] −4.30	.5049	−4.59	.1100	−5.29	.0487	−4.8$_4$
1.0129	−4.14	.5016	−4.06	.1082	−4.42	.0485	−2.0$_4$
1.0017	−4.24	.5099	−4.56	.1046	−4.19	.0449	−7.1$_5$
1.0024	−4.13	.5079	−4.58	.1073	−5.48		
1.0185	−4.17	.5096	−4.28	.1029	−5.09		
		.5043	−4.17			Average	4.25
		.5098	−4.26			S.D.	0.90
		.5150	−4.21			V, %	21

[a] Five 1-g samples dissolved consecutively in a single calorimeter charge.
[b] Ten 1/2-g samples dissolved consecutively in a single calorimeter charge.
[c] Seven 0.1-g samples dissolved consecutively in a single calorimeter charge.
[d] 0.71 g of K_2O·23CaO·12SiO_2 predissolved for each determination.

TABLE 4. *Heat of solution of* K_2SO_4 (c, 11) *in 600.0 g of nitric-hydrofluoric acid at 25° C.*

(11 ml of 48% HF and 587 g of 2.000 *N* HNO_3)

Sample weight	Heat of solution	Sample weight	Heat of solution [a]	Sample weight	Heat of solution [a]	Sample weight	Heat of solution [a]
g	*cal/g*	*g*	*cal/g*	*g*	*cal/g*	*g*	*cal/g*
2.0708	−43.56	0.1076	−44.89	0.1038	−43.66	0.0609	−40.5
1.0265	−43.65	.1063	−44.23	.1016	−43.05	.0612	−41.5
0.5109	−44.40	.1079	−44.64	.1095	−41.26	.0603	−41.7
				.1028	−43.90	.0575	−42.2
				.1073	−43.60	.0595	−43.4
						.0600	−43.5
		Average	−44.59		−43.09		−42.6
		S.D.	0.19		0.48		0.25
		V, %	0.43		1.1		0.59

[a] 0.70 g 2CaO·SiO_2 predissolved for each determination.

TABLE 5. *Heat of solution at 25° C. of* $2CaO \cdot SiO_2$ *(c, β) and* K_2O–CaO–SiO_2 *solid solutions in 600.0 g of nitric-hydrofluoric acid*

(11 ml of 48% HF and 587 g of 2.000 *N* HNO_3)

β−$2CaO \cdot SiO_2$[a]		A		B		C	
Sample weight	Heat of solution	Sample weight	Heat of solution	Sample weight	Heat of solution	Sample weight	Heat of solution
g	*cal/g*	*g*	*cal/g*	*g*	*cal/g*	*g*	*cal/g*
0.7001	565.3	0.7315	566.2	0.7131	568.8	0.7231	568.3
.7013	565.1	.7013	567.0	.7200	568.4	.7300	567.3
.7080	564.3	.7071	565.9	.7121	567.3	.7227	566.4
.7013	564.9	.7110	565.4	.7105	568.2	.7216	569.4
.7031	564.0	.7065	566.6	.7106	568.0	.7217	568.3
.7066	564.9					.7218	568.7
.6960	565.6					.7205	569.1
.7025	564.4						
Average	564.8		566.2		568.1		568.2
S.D	0.19		0.28		0.25		0.40
V, %	0.034		0.049		0.044		0.070
D		E		F		G	
0.7466	568.3	0.7969	567.1	0.7714	568.0	0.7143	568.0
.7497	565.0	.7930	566.7	.7760	568.2	.7169	568.4
.7475	568.4	.7888	565.1	.7680	567.4	.7158	569.0
.7440	568.7	.7985	566.1	.7671	569.5	.7125	566.8
.7450	570.2	.7923	566.2	.7698	567.9	.7087	568.5
.7433	568.5	.7950	567.3	.7663	568.8	.7410	570.3
.7442	568.9	.7942	568.3	.7672	568.1	.7468	569.9
						.7407	572.6
						.7401	570.1
						.7461	569.2
Average	568.3		566.7		568.3		569.3
S.D	0.60		0.38		0.26		0.50
V, %	0.11		0.067		0.046		0.088

[a] Weighed in platinum crucible, heated 3½ hr at 1,050° C, cooled in a desiccator, and reweighed before introduction.

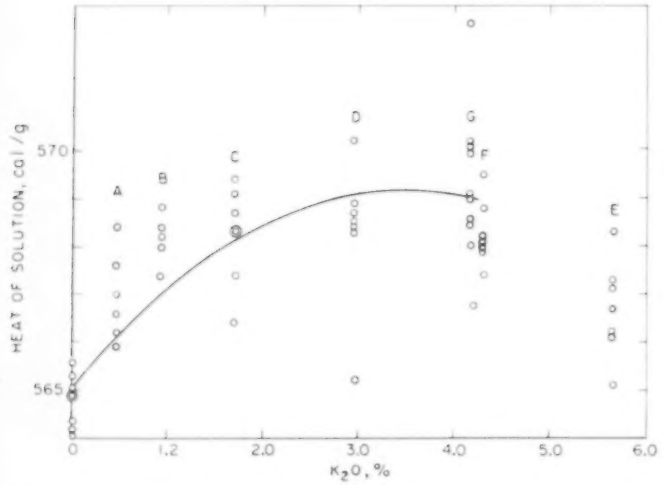

FIGURE 1. *Heats of solution of potassium-calcium-silica solid solutions.*

The heat of solution of $CaSO_4$ (table 3) does not seem to be significantly affected by sample size or by the presence of predissolved $KC_{23}S_{12}$. However, the average value -4.25 ± 0.90 cal/g obtained using the 0.049-g samples was used in calculation. The standard deviation was large, as was expected for small samples, but the average value is about the same as determined for larger samples without predissolving the silicate. The experimental values are substantially different than the calculated [11] heat of solution of $CaSO_4$ in water to form $CaSO_4 \cdot 100000H_2O$ (0.045 g $CaSO_4$/600 g H_2O). +30.1 cal/g, or the value calculated by Brunauer et al. [10] for the heat of solution in nitric-hydrofluoric acid, +31.2 cal/g [10].

The endothermic heat of solution of K_2SO_4 seemed to increase slightly with decrease in sample size (table 4). The presence of predissolved C_2S also seemed to have a slight effect which a *t*-test [12] showed to be significant at the 5-percent level (comparing the two sets of measurements made with 0.1 g samples, $t=2.65$, $t_{crit.}=2.447$). For the calculation of $-\Delta H$ of reaction 1, the value -42.6 ± 0.25 cal/g obtained with 0.06-g samples was used for the heat of solution of potassium sulfate. The calculated value of the heat of solution of K_2SO_4 in water to form $K_2SO_4 \cdot 1000000\ H_2O$ (0.058 g K_2SO_4/600 g H_2O) is −32.9 cal/g [11].

The standard value of 256.6 cal/g for the heat of solution of zinc oxide in the nitric-hydrofluoric acid mixture at 25°C [4,9] was obtained as the result of tests made with the present calorimeter (using a shorter galvanometer-scale distance) [13] combined with the measurements of Stenzel and Morris [14] at 30° C. The values 257.0 ± 0.48 and $256.91 \pm .06$ cal/g given in table 2 for ZnO/solution ratios of 0.2/600 and 1.58/600, respectively, agree well with the standard value for which the calculated ratio is 9.88/600. These three values of the heat of solution of zinc oxide lie very close to the line $y=257.0 - 23.5\ x$, where y is the heat of solution of zinc oxide in calories per gram, and x is the zinc-oxide per solution weight ratio. Values calculated from this equation can safely be used to calibrate the calorimeter for temperature rises smaller than the 4.5° for which the standard value is given.

4. Heats of Formation

The heat of reaction (ΔH) of eq (1) at 25° C is calculated to be -36.3 ± 1.4 kcal, using the heats of solution given in section 3 and the 1952 atomic weights [15]. The heats of formation of $2CaO \cdot SiO_2(c,\beta)$, $CaSO_4$ (c, anhydrite), and $K_2SO_4(c,II)$ are -538.0, -342.42, and -342.66 kcal/mole respectively, at 25° C [11]. The heat of formation of $K_2O \cdot 23CaO \cdot 12SiO_2(c)$, therefore, is -6420 kcal/mole.

5. Summary

The heats of solution of $2CaO \cdot SiO_2(c,\beta)$, $CaSO_4(c)$, $K_2SO_4(c,II)$, and $K_2O \cdot 23CaO \cdot 12SiO_2(c)$ were determined in a mixture of 2.000 N nitric acid and 48-percent hydrofluoric acid in an isothermal-jacket calorimeter. From these and other data in the literature, the heat of formation of $K_2O \cdot 23CaO \cdot 12SiO_2(c)$ from the elements was calculated to be -6420 kcal/mole at 25° C.

WASHINGTON, January 6, 1959.

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Heat of Formation of Boron Trichloride

Walter H. Johnson, Richard G. Miller,[1] and Edward J. Prosen

The heat of formation of gaseous boron trichloride has been determined by the direct reaction of gaseous chlorine with amorphous boron in a calorimeter.

$$B(amorph) + 3/2\ Cl_2(gas) = BCl_3(gas)$$

$$\Delta Hf°(25° C) = -407.98 \pm 1.34 \text{ kj/mole } (-97.51 \pm 0.32 \text{ kcal/mole}).$$

By utilizing the values previously reported for the heats of formation of boric acid, diborane, and pentaborane, the heat of hydrolysis of boron trichloride and the heats of reaction of diborane and pentaborane with chlorine have been obtained. By the use of an estimated value for the heat of sublimation of boron, the average bond energy of the B–Cl bond in boron trichloride is found to be 105.2 kcal at 0° K. The data on the heats of formation of diborane, boric oxide, boric acid, and boron trichloride now form a consistent set of values.

1. Introduction

The heat of formation of boron trichloride has long been uncertain because of the fact that calculation of it has been dependent upon uncertain values of the heat of formation of boric oxide or boric acid. Since new values have been determined for the heat of formation of boric oxide through the heat of decomposition of diborane [1] [2] and the heat of reaction of diborane with water [2], it seemed desirable to make a direct determination of the heat of formation of boron trichloride. This latter value, when combined with the heat of hydrolysis of boron trichloride and with auxiliary data, yields an independent value for the heat of formation of boric oxide. The consistency in the values thus obtained is very strong evidence for the accuracy of the heats of formation of boric oxide, boric acid, diborane, and boron trichloride.

An accurate value for the heat of formation of BCl_3 provides useful information regarding the energy of the B-Cl bond and permits the calculation of the heat of reaction of boron hydrides with chlorine.

2. Method

The substitution method of calorimetry was used. The quantity of electrical energy required to produce a certain rise in the temperature of the calorimeter system was determined in one series of experiments. In a second series the temperature rise was duplicated, but a substantial part of the energy was derived from a precisely measured quantity of the chemical reaction. The calorimeter system was identical in both series except for the reacting chemicals. By this method the energy liberated by the chemical reaction is obtained directly in terms of electrical energy.

[1] Present address: Union Carbide & Carbon Corp., New York, N.Y.
[2] Figures in brackets indicate the literature references at the end of this paper.

3. Materials and Apparatus

The boron was prepared by the thermal decomposition of diborane by passing diborane diluted with helium through a quartz tube heated to 600° C [1]. The amorphous boron was removed from the tube, placed in a tantalum combustion boat, and heated for 1 hr at about 700° C at a pressure of less than 1×10^{-5} mm of mercury. Spectrochemical examination of the boron by the Spectrochemistry Section of the Bureau showed only negligible traces of metal impurities. The effect of a small amount of hydrogen remaining in the boron was calculated to be less than the estimated uncertainty of the measurements.

The chlorine, obtained from the Matheson Company, was about 99 percent pure; the chief impurity was 0.9 percent of carbon dioxide. It was dried by passing over phosphorus pentoxide. The helium was purified by heating it to 600° C in a copper-oxide furnace and directing it successively through Ascarite, anhydrous magnesium perchlorate, and phosphorus pentoxide.

A section of the calorimetric vessel is shown in figure 1. It consisted of a quartz tube A closed at the bottom and fitted with a manganin heating coil B surrounded by a silver shield C and a vacuum jacket D. The boron sample was placed in the quartz crucible E, and the chlorine introduced through the quartz tube F. The exit gases passed through the glass helix G, in which they were cooled to calorimeter temperature.

The calorimeter was of the isothermal jacket type described in a previous paper [2]. Calorimeter temperatures were measured by means of a platinum resistance thermometer in conjunction with a G–2 Mueller bridge and a galvanometer of high sensitivity. Readings on the galvanometer scale were made to the nearest 0.5 mm which was equivalent to 50 μdeg C. The electrical energy was obtained from a 120-v storage battery from which no other current was drawn during these experiments. The quantity

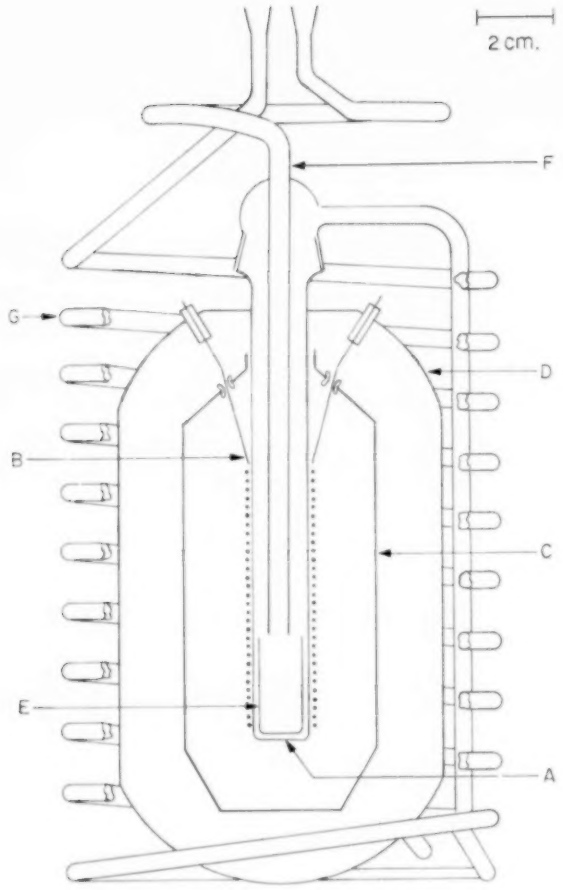

FIGURE 1. *Calorimetric reaction vessel.*

of electrical energy was determined from the electrical current through the heating coil, the potential drop across the coil and the time of passage of the current. The current and potential measurements were obtained from the potential drop across appropriate standard resistors included in the power circuit. The potentials were measured with a Wenner potentiometer which was balanced against a thermostated Weston standard cell [3]. Timing of the experiments was accomplished by reference to the standard second signals produced at the Bureau. All equipment was calibrated in the Bureau laboratories.

4. Procedure

A sample, 0.25 to 0.50 g, of the finely divided amorphous boron was pressed into a pellet, placed in the weighed quartz crucible, and the apparatus assembled. A constant stream of helium was passed through the system during the entire experiment. After the initial rating period, during which temperatures were observed at regular intervals, the vessel was heated electrically to about 400° C and the chlorine introduced. The reaction started and proceeded smoothly. When the desired calorimeter temperature was reached the electric current was interrupted, the chlorine bypassed, and the system allowed to come to equilibrium. Temperatures were then observed at regular intervals during a final rating period.

The rates of flow of the helium and chlorine were determined with capillary flowmeters. The temperatures of the chlorine and helium were taken as the mean room temperatures during the time of flow. The flow rates and temperatures of the chlorine and helium were required only for making the small heat capacity correction. The amount of chemical reaction was determined from the difference between the mass of boron sample and that of the residue remaining in the crucible at the end of the experiment.

The system was calibrated in the same manner except for the omission of the boron and chlorine. In each case the quantity of electrical energy was carefully measured and the initial and final temperatures of the calorimeter were reproduced as closely as possible.

5. Results

The results of the electrical calibration experiments are given in table 1. E is the electrical energy added to the system. ΔRc is the temperature rise corrected for heat leakage and heat of stirring and expressed in ohms increase in resistance of the platinum resistance thermometer as measured on the resistance bridge. E_s is the energy equivalent of the calorimeter expressed in joules/ohm.

TABLE 1. *Results of the electrical calibration experiments*

Experiment number	ΔRc	E	E_s
	ohm	*j*	*j/ohm*
1	0.286106	59088.3	206526
2	.286667	59161.3	206376
3	.284978	58829.9	[a] 206373
4	.287584	59334.5	206321
Mean			206399
Standard deviation of the mean			±44

[a] This value includes a correction of −64.0 j/ohm because of a change in the calorimetric system.

The results of the calorimetric reaction experiments are given in table 2 where ΔRc is the corrected temperature rise of the calorimeter system, q, the product of E_s and ΔRc, is the total heat absorbed by the system, E is the electrical energy added, q_g is the correction for the heat capacities of the re-

TABLE 2. *Results of the calorimetric reaction experiments*

Experiment number	ΔRc	q	E	q_g	Boron reacted	$-\Delta$Hf (25° C)
	Ohm	*j*	*j*	*j*	*g*	*kj/mole*
1	0.287323	59303.2	49172.7	−0.4	0.26876	407.86
2	.302977	62534.1	46119.0	−2.8	.43684	406.65
3	.291356	60135.6	47954.0	−3.5	.32216	409.24
4	.305570	63065.2	44643.5	−5.8	.48890	407.83
Mean						407.90
Standard deviation of the mean						±0.53

actants and products in converting to the isothermal process at 25° C, and $-\Delta Hf$ is the heat evolved by the chemical reaction at 25° C.

The mean value for the heat of reaction as given in table 2 was converted to kcal/mole, using 10.82 for the atomic weight of boron and 4.1840 j as the equivalent of 1 cal. A correction of 0.02 kcal/mole was applied to convert the gases to their thermodynamic standard states. The following heat of reaction was obtained:

$$B(amorph) + 3/2\ Cl_2(gas) = BCl_3\ (gas), \qquad (1)$$

$$\Delta H^\circ_{298.15} = -407.98 \pm 1.34\ kj/mole,$$
$$= -97.51 \pm 0.32\ kcal/mole.$$

The uncertainty has been taken as twice the standard deviation of the mean of the experimental values combined with reasonable estimates of all known sources of error.

6. Derived Data

By the use of the heat of transition of crystalline to amorphous boron as 0.4 kcal/mole (estimated [4]), we obtain for the heat of formation of boron trichloride from crystalline boron:

$$B(cryst) + 3/2\ Cl_2\ (gas) = BCl_3\ (gas), \qquad (2)$$

$$\Delta H^\circ_{298.15} = -406.31 \pm 1.34\ kj/mole,$$
$$= -97.11 \pm 0.32\ kcal/mole.$$

By the combination of (1) and (2) with the heat of vaporization of boron trichloride (5.6 ± 0.1 kcal/mole [4]) there is obtained for the liquid:

$$B(amorph) + 3/2\ Cl_2\ (gas) = BCl_3\ (liquid), \qquad (3)$$

$$\Delta H^\circ_{298.15} = -431.41 \pm 1.42\ kj/mole,$$
$$= -103.11 \pm 0.34\ kcal/mole,\ and$$

$$B(cryst) + 3/2\ Cl_2\ (gas) = BCl_3\ (liq), \qquad (4)$$

$$\Delta H^\circ_{298.15} = -429.74 \pm 1.42\ kj/mole,$$
$$= -102.71 \pm 0.34\ kcal/mole.$$

By combination of the value obtained for eq (1) with the values recently reported from our laboratory for the heat of decomposition of diborane ($\Delta H = -6.73 \pm 0.52$ kcal/mole [1]), its heat of reaction with water ($\Delta H = -111.46 \pm 0.54$ kcal/mole [2]), and with the heat of formation of aqueous hydrochloric acid ($HCl \cdot 1000H_2O$; $\Delta Hf^\circ = -39.808 \pm 0.010$ kcal/mole [6]), we obtain for the heats of hydrolysis of boron trichloride:

$$BCl_3(gas) + 4003\ H_2O(liq) = [H_3BO_3 + 1000\ H_2O]\ (soln) + 3\ [HCl + 1000\ H_2O]\ (soln), \qquad (5)$$

$$\Delta H^\circ_{298.15} = -310.79 \pm 1.84\ kj/mole,$$
$$= -74.28 \pm 0.44\ kcal/mole,\ and$$

$$BCl_3\ liq) + 4003\ H_2O(liq) = [H_3BO_3 + 1000\ H_2O]\ (soln) + 3\ [HCl + 1000\ H_2O]\ (soln), \qquad (6)$$

$$\Delta H^\circ_{298.15} = -287.36 \pm 1.84\ kj/mole,$$
$$= -68.68 \pm 0.44\ kcal/mole.$$

By combining the value recently obtained for the heats of decomposition of diborane and pentaborane [1] with the value from the present investigation and the heat of formation of gaseous hydrogen chloride [6], we obtain for the heats of reaction of diborane and pentaborane with chlorine:

$$B_2H_6\ (gas) + 6Cl_2\ (gas) = 2BCl_3\ (gas) + 6HCl\ (gas), \qquad (7)$$

$$\Delta H^\circ_{298.15} = -1398.00 \pm 2.89\ kj/mole,$$
$$= -334.13 \pm 0.69\ kcal/mole,\ and$$

$$B_5H_9\ (gas) + 12\ Cl_2\ (gas) = 5BCl_3\ (gas) + 9\ HCl\ (gas), \qquad (8)$$

$$\Delta H^\circ_{298.15} = -2925.08 \pm 3.43\ kj/mole,$$
$$= -699.11 \pm 0.82\ kcal/mole.$$

We have combined the value given for eq (2) with the following values for $H^\circ_{298.15} - H^\circ_0$ in kcal/mole:

BCl_3 (gas)	3.362	[7]
B(cryst)	0.290	[7]
Cl_2 (gas)	2.194	[8]

and have obtained −96.89 kcal/mole for the heat of formation of BCl_3 (gas) at 0° K.

The heat of sublimation of boron has been calculated from vapor pressure data [9] to be 133 ± 4 kcal/mole at 0° K. If the heat of dissociation of Cl_2 (gas) is taken as 57.08 kcal/mole [8], these data give for the reaction:

$$B\ (gas) + 3Cl\ (gas) = BCl_3\ (gas), \qquad (9)$$
$$\Delta H^\circ_0 = -315.51\ kcal/mole,$$

from which the average bond energy is calculated to be 105.2 kcal.

7. Prior Investigations

In the following treatment of the previously reported data, several corrections have been applied to reduce the data to a comparable basis. The data for the hydrolysis reaction (eq 6) have been converted to 25° C with an estimated temperature coefficient of −150 cal/deg mole. The heats of formation of HCl and H_3BO_3 in the resulting solution have been taken as those of the aqueous acids of the same concentration [6]; this assumes that the heat of mixing of these acids is negligible at high dilutions [10, 11, 12]. For ease in comparison, the tabulated heats of hydrolysis have been corrected to final concentrations of $H_3BO_3 \cdot 1000H_2O$ and $HCl \cdot 1000H_2O$. All values are based on the 1956 International Atomic Weights [13].

Troost and Hautefeuille [14] passed chlorine over amorphous boron and hydrolyzed the resulting BCl_3. In a separate experiment they hydrolyzed liquid BCl_3 to a solution of the same final composition (H_3BO_3·3HCl·900H_2O). For the first reaction they report as the mean of six experiments: $\Delta H = -183.2$ kcal/mole BCl_3; for the second, $\Delta H = -79.2$ kcal/mole. No details are given by Troost and Hautefeuille as to the temperature at which they carried out their experiments, however they used the same mercury calorimeter as Favre and Silberman [15] and apparently used the same conditions. Favre and Silberman also do not specify their working temperatures but there are some indications in their papers that it was about 20° C. We have assumed this to be the case; thus, the values obtained by Troost and Hautefeuille corrected to the specified conditions give $\Delta H = -183.7$ kcal/mole for the formation reaction and $\Delta H = -80.0$ kcal/mole for the hydrolysis reaction. The standard heats of formation of BCl_3 (based on crystalline boron as the standard state) calculated from these data are −103.3 kcal/mole for the direct combination and −91.4 kcal/mole for the hydrolysis method.

Considerable doubt has been cast upon these data from the observations by Berthelot [16] and Thomsen [17] that Favre and Silberman obtained values for the heats of neutralization of hydrochloric, hydrobromic, hydriodic, and nitric acids by both potassium and sodium hydroxides that were much higher than the accepted values, although exhibiting reasonable concordance among themselves. This suggests that there was some systematic error, probably in their calibration. An examination of their data [15] for these, as well as for other reactions indicates that the reported values should be reduced by about 11 percent. If Troost and Hautefeuille used the same calorimetric system with the same calibration, which they imply, then the same correction should be applied to their data. This would reduce the value for the heat of formation of BCl_3 (liq) obtained from the combination of the two reactions to −91.9 kcal/mole. The heat of hydrolysis then becomes −71.2 kcal/mole, which leads to −100.2 kcal/mole for the heat of formation of liquid BCl_3. This correction is admittedly only approximate and the values so obtained are quite uncertain.

There is no information regarding the purity of the amorphous boron used by Troost and Hautefeuille; however, the boron available at that time was undoubtedly quite impure. On the other hand, reasonably pure BCl_3 could be prepared; for this reason their data for the hydrolysis reaction should be more reliable than that which they obtained from the direct combination.

Berthelot [16] obtained −65.8 kcal/mole for the heat of hydrolysis of liquid BCl_3 at 10° C. When corrected for temperature and concentration the heat of hydrolysis becomes −68.6 kcal/mole, which gives −103.2 kcal/mole for the heat of formation of liquid BCl_3.

Laubengayer and Sears [18] studied the same reaction at 0° C in an ice calorimeter and reported two values for different final concentrations. Both values, when corrected for temperature and concentration, give −69.3 kcal/mole for the heat of hydrolysis and −102.1 kcal/mole for the heat of formation of liquid BCl_3.

Kapustinskiĭ and Samoĭlov [19] have measured the heat of solution and hydrolysis of gaseous BCl_3 at 25° C. Their data give −90.7 kcal/mole for the heat of formation of BCl_3 (gas).

Skinner and Smith [20] determined the heat of hydrolysis of liquid BCl_3 at 25° C to be −69.2 kcal/mole, which gives −102.2 kcal/mole for the heat of formation.

Lacher, Scruby, and Park [21] measured the heat of reaction for the gas-phase chlorination of diborane, to yield BCl_3 and HCl at about 80° C. We have corrected this value to 25° C and obtained for the reaction:

$$6Cl_2(gas) + B_2H_6(gas) = 2BCl_3(gas) + 6HCl(gas), \quad \Delta H = -342.9 \text{ kcal/mole}.$$

This leads to −101.5 kcal/mole for the heat of formation of BCl_3(gas).

The values for the heats of hydrolysis and the corresponding standard heats of formation of liquid BCl_3 are summarized in table 3. The crystalline form of boron at 25° C has been taken as the standard reference state. Values reported for the heat of formation of BCl_3(gas) have been converted to correspond to the liquid using 5.6 kcal/mole [5] for the heat of vaporization. It is apparent that the agreement among the results of Berthelot, Laubengayer and Sears, Skinner and Smith, and the present investigation is good.

TABLE 3. *Heats of hydrolysis and formation of BCl_3 (liquid)*

Investigators	ΔH hydrolysis	ΔHf°
	kcal/mole	*kcal/mole*
Troost and Hautefeuille [14]:		
Direct reaction	−80.0	−103.3
Hydrolysis		−91.4
Direct reaction, corrected		−91.9
Hydrolysis, corrected	−71.2	−100.2
Berthelot [16]	−68.2	−103.2
Laubengayer and Sears [18]	−69.3	−102.1
Kapustinskiĭ and Samoĭlov [19]	−75.1	−96.3
Skinner and Smith [20]	−69.2	−102.2
Lacher, Scruby, and Park [21]		−107.1
Present investigation		−102.7

8. Discussion

Most of the thermochemistry of the boron compounds involves the heat of formation of boric oxide (or of boric acid); a reliable value for this constant is therefore quite important. As we have stated previously [2], values reported for the heat of formation of boric oxide range from −280 to −370 kcal/mole. Most of these values were obtained by the combustion of amorphous boron in an oxygen bomb calorimeter; the difficulties and unreliability of such experiments have been analyzed [2]. Nathan [22] obtained -306 ± 3 kcal/mole for the complete combustion of boron in an oxygen bomb calorimeter. We have obtained -305.3 ± 0.8 kcal/mole for the standard heat of formation of boric oxide from the

heat of decomposition of diborane and the heat of reaction of diborane with water [2]. The latter value is in reasonably good agreement with that reported by Roth, Börger, and Bertram [23].

An independent value for the heat of formation of boric oxide may be obtained from the heat of chlorination of boron and the heat of hydrolysis of the resulting BCl_3. The only previous data leading to a value for the heat of formation of BCl_3 that do not involve boric oxide are those of Troost and Hautefeuille, discussed above. The uncertainties regarding their materials, apparatus, and calibration make this value very unreliable.

We have determined directly the heat of formation of BCl_3 to obtain an independent value for the heat of formation of B_2O_3, and to resolve the discrepancy in the values reported for the heat of formation of BCl_3. If the value for the heat of formation of BCl_3 obtained in this investigation is combined with the heat of hydrolysis reported by Skinner and Smith [20], there is obtained -306.3 kcal/mole for the standard heat of formation of boric oxide. This is in good agreement with the value obtained from the diborane data.

In view of the general agreement among the values obtained by different methods it can be stated that the data available for the heats of formation of diborane, boric oxide, boric acid, and boron trichloride form a consistent set of values.

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WASHINGTON, January 21, 1959.

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Beginning in July 1959, the Journal of Research will be published in four separate sections which may be subscribed for individually. This change is being made to provide a publication whose subject matter concentrates on particular fields of interest, thus meeting the specialized needs of individual scientists, engineers, and mathematicians.

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